

ALAGAPPA UNIVERSITY



[Accredited with 'A+' Grade by NAAC (CGPA:3.64) in the Third Cycle
and Graded as Category–I University by MHRD-UGC]

(A State University Established by the Government of Tamil Nadu)

KARAIKUDI – 630 003

Directorate of Distance Education

M.Sc. [Physics]

IV - Semester

345 43

MATERIALS SCIENCE

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Vikas Publishing House, Units: (1, 3, 4.0-4.3, 4.7-4.11, 6.6-6.13, 7.3, 7.5-7.9, 8, 9, 11, 12.4-12.10, 13.5, 13.7-13.12, 14)



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VIKAS® PUBLISHING HOUSE PVT. LTD.
E-28, Sector-8, Noida - 201301 (UP)
Phone: 0120-4078900 • Fax: 0120-4078999
Regd. Office: A-27, 2nd Floor, Mohan Co-operative Industrial Estate, New Delhi 1100 44
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Work Order No.AU/DDE/DE12/Printing of Course Material/2020 Dated 06.05.2020 Copies - 100

SYLLABI-BOOK MAPPING TABLE

Materials Science

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Unit 12 - Smart Materials
Amorphous and Glassy Materials, Structure, Preparation Methods and Novel Properties.
Unit 13 - Applications of Smart Materials
Shape Memory Alloys, Working Mechanism, Pseudo Elasticity, Applications, Nickel-Titanium (Nitinol) Alloys, Material Characteristics of Nitinol.
Unit 14 - Micro Electro Mechanical Systems
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INTRODUCTION

The interdisciplinary field of 'Materials Science', also commonly termed 'Materials Science and Engineering', explains the design and discovery of new materials, particularly solids. The academic origins of materials science branch started when researchers began to use analytical thinking from chemistry, physics, and engineering to understand ancient, phenomenological observations in metallurgy and mineralogy.

Principally, 'Materials Science' is the study of the properties of solid materials and how those properties are determined by a material's composition and structure. The different materials are studied and applied in materials science and are usually divided into four categories, namely metals, polymers, semiconductors, and ceramics. Semiconductors, metals, and ceramics are used today to form highly complex systems, such as integrated electronic circuits, optoelectronic devices, and magnetic and optical mass storage media. These materials form the basis of our modern computing world, and hence research into these materials is of vital importance. Polymers are chemical compounds made up of a large number of identical components linked together resembling chains. They are an important part of materials science. Polymers are the raw materials (the resins) used to make what are commonly called plastics and rubber. With a basic understanding of the origins of properties, materials can be selected or designed for an enormous variety of applications, ranging from structural steels to computer microchips. Materials science is therefore important to engineering activities, such as electronics, aerospace, telecommunications, information processing, nuclear power, and energy conversion.

Materials scientists emphasize on how the history of a material (processing) influences its structure, and thus the material's properties and performance. The understanding of processing-structure-properties relationships is called the materials paradigm. This paradigm is typically used in a variety of advance research areas including nanotechnology, biomaterials and metallurgy.

In addition, materials science is also a significant part of forensic engineering and failure analysis – investigating materials, products, structures or components, which fail or do not function as intended, causing personal injury or damage to property. Such investigations are key to understanding, for example, the causes of various aviation accidents and incidents.

This book, *Materials Science*, is divided into four blocks, which are further subdivided into fourteen units. This book provides a basic understanding of the subject and helps to grasp its fundamentals. In a nutshell, it explains various aspects, such as elastic, inelastic and viscoelastic behaviour of material, polymers, structure and properties, addition and condensation polymerization, polymer types, applications of polymers, corrosion and oxidation of metals, kinetic theory of gases, gas transport and pumping, vacuum pumps, diffusion and turbo molecular pumps, Pirani and Penning gauges, thin films by thermal evaporation, thickness measurement,

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quartz crystal method, thin films by epitaxy and its applications, principles of Laser, resonators, Q-switching and mode locking, types of Laser, non-linear optical properties of materials, composite materials and its applications, smart materials, amorphous and glassy materials, applications of smart materials, Nickel-Titanium (Nitinol) alloys, Micro Electro Mechanical Systems (MEMS), silicon, porous silicon and silicon oxide based MEMS, fabrication of piezoelectric and piezoresistive MEMS materials, micro-actuators and micro-accelerometers.

The book follows the Self-Instructional Mode (SIM) wherein each unit begins with an 'Introduction' to the topic. The 'Objectives' are then outlined before going on to the presentation of the detailed content in a simple and structured format. 'Check Your Progress' questions are provided at regular intervals to test the student's understanding of the subject. 'Answers to Check Your Progress Questions', a 'Summary', a list of 'Key Words', and a set of 'Self-Assessment Questions and Exercises' are provided at the end of each unit for effective recapitulation.

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BLOCK - I
MATERIAL BEHAVIOUR

UNIT 1 ELASTIC BEHAVIOUR OF MATERIAL

Structure

1.0 INTRODUCTION

In physics and materials science, elasticity is the ability of a body to resist a distorting influence and to return to its original size and shape when that influence or force is removed. Solid objects will deform when adequate loads are applied to them, if the material is elastic, the object will return to its initial shape and size after removal. This is in contrast to plasticity, in which the object fails to do so and instead remains in its deformed state. The physical reasons for elastic behaviour can be quite different for different materials. In metals, the atomic lattice changes size and shape when forces are applied (energy is added to the system). When forces are removed, the lattice goes back to the original lower energy state. For rubbers and other polymers, elasticity is caused by the stretching of polymer chains when forces are applied.

Hooke's law states that the force required to deform elastic objects should be directly proportional to the distance of deformation, regardless of how large that distance becomes. This is known as perfect elasticity, in which a given object will return to its original shape no matter how strongly it is deformed. This is an ideal concept only; most materials which possess elasticity in practice remain purely elastic only up to very small deformations, after which plastic (permanent) deformation occurs.

In engineering, the elasticity of a material is quantified by the elastic modulus such as the Young's modulus, bulk modulus or shear modulus which measure the amount of stress needed to achieve a unit of strain, a higher modulus indicates that the material is harder to deform. The SI unit of this modulus is the Pascal (Pa). The

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material's elastic limit or yield strength is the maximum stress that can arise before the onset of plastic deformation. Its SI unit is also the Pascal (Pa).

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials, like water, resist shear flow and strain linearly with time when a stress is applied. Elastic materials strain when stretched and immediately return to their original state once the stress is removed. The ultimate tensile strength of a material is an intensive property; therefore its value does not depend on the size of the test specimen. However, depending on the material, it may be dependent on other factors, such as the preparation of the specimen, the presence or otherwise of surface defects, and the temperature of the test environment and material. Plastic deformation is not undone simply by removing the applied force. An object in the plastic deformation range, however, will first have undergone elastic deformation, which is undone simply be removing the applied force, so the object will return part way to its original shape. Soft thermoplastics have a rather large plastic deformation range as do ductile metals such as copper, silver, and gold. Steel does, too, but not cast iron. Hard thermosetting plastics, rubber, crystals, and ceramics have minimal plastic deformation ranges.

In this unit, you will study about the elastic, inelastic and viscoelastic behaviour of the materials, tensile strength, toughness, and elongation, plastic deformation, hardness, creep and fatigue.

1.1 OBJECTIVES

After going through this unit, you will be able to:

- Describe the elastic behavior of material
- Understand the inelastic and viscoelastic behaviour of material
- Explain the tensile strength, toughness, elongation, plastic deformation, hardness, creep and fatigue

1.2 ELASTIC

Whenever some external system of forces act on a body, it undergoes some deformation. The deformation increases as the forces increase. If a material regains its original position on the removal of the external forces, it is called an elastic material.

The physical reasons for elastic behaviour can be quite different for different materials. In metals, the atomic lattice changes size and shape when forces are applied (energy is added to the system). When forces are removed, the lattice goes back to the original lower energy state. For rubbers and other polymers, elasticity is caused by the stretching of polymer chains when forces are applied.

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When an elastic material is deformed due to an external force, it experiences internal resistance to the deformation and restores it to its original state if the external force is no longer applied. There are various elastic moduli, such as Young's modulus, the shear modulus, and the bulk modulus, all of which are measures of the inherent elastic properties of a material as a resistance to deformation under an applied load. The various moduli apply to different kinds of deformation. For instance, Young's modulus applies to extension/compression of a body, whereas the shear modulus applies to its shear. Young's modulus and shear modulus are only for solids, whereas the bulk modulus is for solids, liquids, and gases.

The elasticity of materials is described by a stress–strain curve, which shows the relation between stress (the average restorative internal force per unit area) and strain (the relative deformation). The curve is generally nonlinear, but it can (by use of a Taylor series) be approximated as linear for sufficiently small deformations (in which higher-order terms are negligible). If the material is isotropic, the linearized stress–strain relationship is called Hooke's law, which is often presumed to apply up to the elastic limit for most metals or crystalline materials whereas nonlinear elasticity is generally required to model large deformations of rubbery materials even in the elastic range. For even higher stresses, materials exhibit plastic behaviour, that is, they deform irreversibly and do not return to their original shape after stress is no longer applied. For rubber-like materials such as elastomers, the slope of the stress–strain curve increases with stress, meaning that rubbers progressively become more difficult to stretch, while for most metals, the gradient decreases at very high stresses, meaning that they progressively become easier to stretch. Elasticity is not exhibited only by solids; non-Newtonian fluids, such as viscoelastic fluids, will also exhibit elasticity in certain conditions quantified by the Deborah number. In response to a small, rapidly applied and removed strain, these fluids may deform and then return to their original shape. Under larger strains, or strains applied for longer periods of time, these fluids may start to flow like a viscous liquid. Because the elasticity of a material is described in terms of a stress–strain relation, it is essential that the terms stress and strain be defined without ambiguity. Typically, two types of relation are considered. The first type deals with materials that are elastic only for small strains. The second deals with materials that are not limited to small strains. Clearly, the second type of relation is more general in the sense that it must include the first type as a special case.

For small strains, the measure of stress that is used is the Cauchy stress while the measure of strain that is used is the infinitesimal strain tensor; the resulting (predicted) material behaviour is termed linear elasticity, which (for isotropic media) is called the generalized Hooke's law. Cauchy elastic materials and hypo elastic materials are models that extend Hooke's law to allow for the possibility of large rotations, large distortions, and intrinsic or induced anisotropy. For more general situations, any of a number of stress measures can be used, and it generally desired (but not required) that the elastic stress–strain relation be phrased in terms of a finite strain measure that is work conjugate to the selected stress measure, i.e., the

time integral of the inner product of the stress measure with the rate of the strain measure should be equal to the change in internal energy for any adiabatic process that remains below the elastic limit.

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Linear Elasticity and Cauchy elastic materials

For small deformations, most elastic materials such as springs exhibit linear elasticity and can be described by a linear relation between the stress and strain. This relationship is known as Hooke's law. A geometry-dependent version of the idea was first formulated by Robert Hooke in 1675 as a Latin anagram, 'Ceiiinosssttuv'. He published the answer in 1678: 'Ut tensio, sic vis' meaning 'As the Extension, so the Force', a linear relationship commonly referred to as Hooke's law. This law can be stated as a relationship between tensile force F and corresponding extension displacement x,

$$F = kx$$

Where k is a constant known as the rate or spring constant.

Cauchy Elastic Materials

It is generally incorrect to state that Cauchy stress is a function of merely a strain tensor, as such a model lacks crucial information about material rotation needed to produce correct results for an anisotropic medium subjected to vertical extension in comparison to the same extension applied horizontally and then subjected to a 90-degree rotation; both these deformations have the same spatial strain tensors yet must produce different values of the Cauchy stress tensor. Even though the stress in a Cauchy-elastic material depends only on the state of deformation, the work done by stresses might depend on the path of deformation. Therefore, Cauchy elasticity includes non-conservative 'Non-Hyper elastic' models (in which work of deformation is path dependent) as well as conservative 'Hyper Elastic Material' models (for which stress can be derived from a scalar 'Elastic Potential' function).

1.3 INELASTIC AND VISCOELASTIC BEHAVIOUR OF MATERIALS

Inelastic

The inelastic behaviour of material, to cross-section, to critical region, and, finally, to the entire structure. In earthquake engineering, inelastic response is probable, and survivability of organisations depends on the ability of the organisation to weather several cycles of fully reversed inelastic deformation without extreme loss of difficulty or strength.

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Inelastic Behaviour of Organisations

From Material
↓
To Cross Section
↓
To Critical Region
↓
To Structure

Inelastic materials, simply put, are non-elastic materials. They do not show a fixed trend of deformation vs applied force; in fact, they might not deform at all (rigid materials) or the deformation observed is not completely recoverable; on removal of the applied force, the material does not return to its original shape, but to a permanent deformed shape. Such materials are called **Plastic** materials.

A characteristic material like steel shows all these forms under changed conditions of loading (applied force). For particularly low magnitudes of forces, it is practically rigid. Increasing magnitudes of force show a linear elastic response, while further increase show a non-linear, plastic response, till rupture occurs when the material breaks.

Viscoelastic

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials, like water, resist shear flow and strain linearly with time when a stress is applied. Elastic materials strain when stretched and immediately return to their original state once the stress is removed.

Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent strain. Whereas elasticity is usually the result of bond stretching along crystallographic planes in an ordered solid, viscosity is the result of the diffusion of atoms or molecules inside an amorphous material.

Depending on the change of strain rate versus stress inside a material, the viscosity can be categorized as having a linear, non-linear, or plastic response. When a material exhibits a linear response it is categorized as a Newtonian material. In this case the stress is linearly proportional to the strain rate. If the material exhibits a non-linear response to the strain rate, it is categorized as Non-Newtonian fluid. There is also an interesting case where the viscosity decreases as the shear/ strain rate remains constant. A material which exhibits this type of behaviour is known as thixotropic. In addition, when the stress is independent of this strain rate, the material exhibits plastic deformation. Many viscoelastic materials exhibit rubber like behaviour explained by the thermodynamic theory of polymer elasticity.

Some examples of viscoelastic materials include amorphous polymers, semi crystalline polymers, biopolymers, metals at very high temperatures, and bitumen materials. Cracking occurs when the strain is applied quickly and outside of the

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elastic limit. Ligaments and tendons are viscoelastic, so the extent of the potential damage to them depends both on the rate of the change of their length as well as on the force applied.

A viscoelastic material has the following properties:

- Hysteresis is seen in the stress–strain curve
- Stress relaxation occurs: step constant strain causes decreasing stress

Check Your Progress

1. Explain the elastic behavior of materials.
2. Write the Cauchy elastic materials.
3. Elaborate on the inelastic materials.
4. Analyse the viscoelastic.

1.4 TENSILE STRENGTH, TOUGHNESS, ELONGATION, PLASTIC DEFORMATION, HARDNESS, CREEP AND FATIGUE

Tensile Strength

Tensile strength is a measurement of the force required to pull something such as rope, wire, or a structural beam to the point where it breaks.

The tensile strength of a material is the maximum amount of tensile stress that it can take before failure, for example breaking.

There are three typical definitions of tensile strength:

- **Yield strength** - The stress a material can withstand without permanent deformation. This is not a sharply defined point. Yield strength is the stress which will cause a permanent deformation of 0.2% of the original dimension.
- **Ultimate strength** - The maximum stress a material can withstand.
- **Breaking strength** - The stress coordinate on the stress-strain curve at the point of rupture.

Typical Tensile Strengths

Typical tensile strengths of some materials			
Material	**Yield strength (MPa)**	**Ultimate strength (MPa)**	**Density (g/cm³)**
Structural steel ASTM A36 steel	250	400	7.8
Steel, API 5L X65 (Fikret Mert Veral)	448	531	7.8
Steel, high strength alloy ASTM A514	690	760	7.8
Maraging_Steel, Grade 350	2400	2500	8.1
Steel Wire			7.8

Steel, Piano wire	c. 2000		7.8
High density polyethylene (HDPE)	26-33	37	0.95
Polypropylene	12-43	19.7-80	0.91
Stainless steel AISI 302 - Cold-rolled	520	860	8.03;
Cast iron 4.5% C, ASTM A-48	130 (??)	200	7.3;
Titanium Alloy (6% Al, 4% V)	830	900	4.51
Aluminium Alloy 2014-T6	400	455	2.7

Note: Multiwall carbon nanotubes have the highest tensile strength of any material yet measured, with labs producing them at a tensile strength of 63 GPa, still well below their theoretical limit of 300 GPa. However, as of 2004, no macroscopic object constructed of carbon nanotubes has had a tensile strength remotely approaching this figure, or substantially exceeding that of high-strength materials like Kevlar.

Toughness

In materials science and metallurgy, toughness is the ability of a material to absorb energy and plastically deform without fracturing. One definition of material toughness is the amount of energy per unit volume that a material can absorb before rupturing. This measure of toughness is different from that used for fracture toughness, which describes load bearing capabilities of materials with flaws. It is also defined as a material's resistance to fracture when stressed.

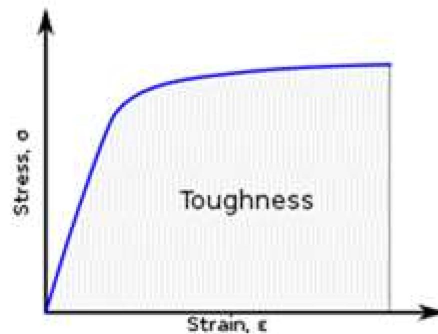


Fig. 1.1 *Toughness as defined by the Area under the Stress-Strain Curve*

In materials science and metallurgy, toughness is the ability of a material to absorb energy and plastically deform without fracturing. One definition of material toughness is the amount of energy per unit volume that a material can absorb before rupturing. This measure of toughness is different from that used for fracture toughness, which describes load bearing capabilities of materials with flaws. It is also defined as a material's resistance to fracture when stressed.

Toughness requires a balance of strength and ductility.

Toughness and Strength

Toughness is related to the area under the stress–strain curve. In order to be tough, a material must be both strong and ductile. For example, brittle materials (like ceramics) that are strong but with limited ductility are not tough, conversely, very ductile materials with low strengths are also not tough. To be tough, a material should withstand both high stresses and high strains. Generally speaking, strength indicates how much force the material can support, while toughness indicates how much energy a material can absorb before rupturing.

Toughness Tests

The toughness of a material can be measured using a small specimen of that material. A typical testing machine uses a pendulum to deform a notched specimen of defined cross-section. The height from which the pendulum fell, minus the height to which it rose after deforming the specimen, multiplied by the weight of the pendulum is a measure of the energy absorbed by the specimen as it was deformed during the impact with the pendulum. The Charpy and Izod notched impact strength tests are typical ASTM tests used to determine toughness.

Unit of Toughness

Tensile toughness or *deformation energy* (U_T) is measured in units of Joule per cubic metre ($J \cdot m^{-3}$) in the SI system and inch-pound-force per cubic inch ($in \cdot lbf \cdot in^{-3}$) in US customary units.

$1.00\ N \cdot m.m^{-3} \simeq 0.000145\ in \cdot lbf \cdot in^{-3}$ and $1.00\ in \cdot lbf \cdot in^{-3} \simeq 6.89\ kN \cdot m.m^{-3}$.

In the SI system, the unit of tensile toughness can be easily calculated by using area underneath the stress–strain ($\sigma - \varepsilon$) curve, which gives tensile toughness value, as given below:

$$U_T = \text{Area Underneath the Stress–Strain } (\sigma - \varepsilon) \text{ Curve} = \sigma \times \varepsilon$$

$$U_T\ [=]\ P/A \times \Delta L/L = (N \cdot m^{-2}) \cdot (\text{Unit Less})$$

$$U_T\ [=]\ N \cdot m \cdot m^{-3}$$

$$U_T\ [=]\ J \cdot m^{-3}$$

Elongation

Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining the change in length from original. Elongation is expressed as a percentage of the original length. Ultimate elongation is the percentage change in length from original to rupture.

Plastic Deformation



Swebor-brand high-strength low alloy steel plate, showing both sides, after plastic deformation from defeating projectiles in ballistics testing. Note: When exposed to fire, steel first expands and then loses its strength, exceeding critical temperature at 538°C or 1000°F per ASTM E119 unless treated with fireproofing.

This type of deformation is not undone simply by removing the applied force. An object in the plastic deformation range, however, will first have undergone elastic deformation, which is undone simply be removing the applied force, so the object will return part way to its original shape. Soft thermoplastics have a rather large plastic deformation range as do ductile metals such as copper, silver, and gold. Steel does, too, but not cast iron. Hard thermosetting plastics, rubber, crystals, and ceramics have minimal plastic deformation ranges. An example of a material with a large plastic deformation range is wet chewing gum, which can be stretched to dozens of times its original length.

Under tensile stress, plastic deformation is characterized by a strain hardening region and a necking region and finally, fracture (also called rupture). During strain hardening the material becomes stronger through the movement of atomic dislocations. The necking phase is indicated by a reduction in cross-sectional area of the specimen. Necking begins after the ultimate strength is reached. During necking, the material can no longer withstand the maximum stress and the strain in the specimen rapidly increases. Plastic deformation ends with the fracture of the material.

Hardness

Hardness is a measure of the resistance to localized plastic deformation induced by either mechanical indentation or abrasion. In general, different materials differ in their hardness; for example hard metals such as titanium and beryllium are harder than soft metals such as sodium and metallic tin, or wood and common plastics. Macroscopic hardness is generally characterized by strong intermolecular bonds,

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but the behaviour of solid materials under force is complex; therefore, there are different measurements of hardness: scratch hardness, indentation hardness, and rebound hardness.

Hardness is dependent on ductility, elastic stiffness, plasticity, strain, strength, toughness, viscoelasticity, and viscosity.

Common examples of hard matter are ceramics, concrete, certain metals, and super hard materials, which can be contrasted with soft matter.

Scratch Hardness



Hardness Tester

There are three main types of hardness measurements: scratch, indentation, and rebound. Within each of these classes of measurement there are individual measurement scales. For practical reasons conversion tables are used to convert between one scale and another.

Scratch Hardness

Scratch hardness is the measure of how resistant a sample is to fracture or permanent plastic deformation due to friction from a sharp object. The principle is that an object made of a harder material will scratch an object made of a softer material. When testing coatings, scratch hardness refers to the force necessary to cut through the film to the substrate. The most common test is Mohs scale, which is used in mineralogy. One tool to make this measurement is the sclerometer.

Another tool used to make these tests is the pocket hardness tester. This tool consists of a scale arm with graduated markings attached to a four-wheeled carriage. A scratch tool with a sharp rim is mounted at a predetermined angle to

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the testing surface. In order to use it a weight of known mass is added to the scale arm at one of the graduated markings, the tool is then drawn across the test surface. The use of the weight and markings allows a known pressure to be applied without the need for complicated machinery.

Indentation Hardness

Indentation hardness measures the resistance of a sample to material deformation due to a constant compression load from a sharp object. Tests for indentation hardness are primarily used in engineering and metallurgy fields. The tests work on the basic premise of measuring the critical dimensions of an indentation left by a specifically dimensioned and loaded indenter.

Common indentation hardness scales are Rockwell, Vickers, Shore, and Brinell, amongst others.

Rebound Hardness

Rebound hardness, also known as dynamic hardness, measures the height of the 'Bounce' of a diamond-tipped hammer dropped from a fixed height onto a material. This type of hardness is related to elasticity. The device used to take this measurement is known as a scleroscope.

Two scales that measures rebound hardness are the Leeb rebound hardness test and Bennett hardness scale.

Ultrasonic Contact Impedance (UCI) method determines hardness by measuring the frequency of an oscillating rod. The rod consists of a metal shaft with vibrating element and a pyramid-shaped diamond mounted on one end.

Creep

In materials science, creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods and generally increases as they near their melting point.

The rate of deformation is a function of the material's properties, exposure time, exposure temperature and the applied structural load. Depending on the magnitude of the applied stress and its duration, the deformation may become so large that a component can no longer perform its function — for example creep of a turbine blade could cause the blade to contact the casing, resulting in the failure of the blade. Creep is usually of concern to engineers and metallurgists when evaluating components that operate under high stresses or

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high temperatures. Creep is a deformation mechanism that may or may not constitute a failure mode. For example, moderate creep in concrete is sometimes welcomed because it relieves tensile stresses that might otherwise lead to cracking.

Unlike brittle fracture, creep deformation does not occur suddenly upon the application of stress. Instead, strain accumulates as a result of long-term stress. Therefore, creep is a "time-dependent" deformation. It works on the principle of Hooke's law (stress is directly proportional to strain).

Fatigue (material)



Fracture of an aluminium crank arm. Dark area of striations: slow crack growth. Bright granular area: sudden fracture.

In materials science, fatigue is the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle, typically producing striations on some parts of the fracture surface. The crack will continue to grow until it reaches a critical size, which occurs when the stress intensity factor of the crack exceeds the fracture toughness of the material, producing rapid propagation and typically complete fracture of the structure.

Fatigue has traditionally been associated with the failure of metal components which led to the term metal fatigue. In the nineteenth century, the sudden failing of metal railway axles was thought to be caused by the metal crystallising because of the brittle appearance of the fracture surface, but this has since been disproved. Most materials seem to experience some sort of fatigue-related failure such as composites, plastics and ceramics.

To aid in predicting the fatigue life of a component, fatigue tests are carried out using coupons to measure the rate of crack growth by applying constant amplitude cyclic loading and averaging the measured growth of a crack over thousands of cycles. However, there are also a number of special cases that need to be considered where the rate of crack growth is significantly different compared

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to that obtained from constant amplitude testing. Such as: the reduced rate of growth that occurs for small loads near the threshold or after the application of an overload; and the increased rate of crack growth associated with short cracks or after the application of an underload.

If the loads are above a certain threshold, microscopic cracks will begin to initiate at stress concentrations such as holes, Persistent Slip Bands (PSBs), composite interfaces or grain boundaries in metals. The stress values that cause fatigue damage are typically much less than the yield strength strength of the material.

Check Your Progress

5. Define the tensile strength.
6. Draw the stress-strain curve of toughness.
7. Elaborate on the elongation.
8. Analyse about the plastic deformation of the materials.
9. What is the scratch hardness?
10. What do you understand by creep and fatigue?

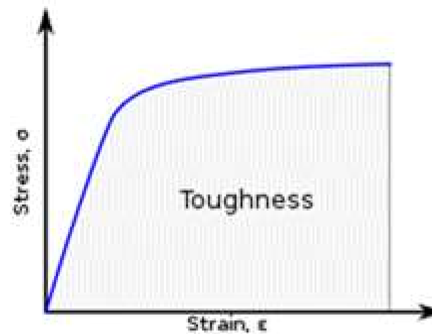
1.5 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Some external system of forces act on a body, it undergoes some deformation. The deformation increases as the forces increase. If a material regains its original position on the removal of the external forces, it is called an elastic material.
2. Cauchy elasticity includes non-conservative 'Non-Hyper elastic' models (in which work of deformation is path dependent) as well as conservative 'Hyper Elastic Material' models (for which stress can be derived from a scalar 'Elastic Potential' function).
3. The inelastic behaviour of material, to cross-section, to critical region, and, finally, to the entire structure. In earthquake engineering, inelastic response is probable, and survivability of organisations depends on the ability of the organisation to weather several cycles of fully reversed inelastic deformation without extreme loss of difficulty or strength.
4. Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials,

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like water, resist shear flow and strain linearly with time when a stress is applied.

5. Tensile strength is a measurement of the force required to pull something, such as rope, wire, or a structural beam to the point where it breaks. The tensile strength of a material is the maximum amount of tensile stress that It can take before failure, for example breaking.
6. Toughness is defined by the area under the stress-strain curve as shown below.



7. Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining the change in length from original. Elongation is expressed as a percentage of the original length. Ultimate elongation is the percentage change in length from original to rupture.
8. This type of deformation is not undone simply by removing the applied force. An object in the plastic deformation range, however, will first have undergone elastic deformation, which is undone simply be removing the applied force, so the object will return part way to its original shape.
9. Scratch hardness is the measure of how resistant a sample is to fracture or permanent plastic deformation due to friction from a sharp object. The principle is that an object made of a harder material will scratch an object made of a softer material when testing coatings, scratch hardness refers to the force necessary to cut through the film to the substrate. The most common test is Mohs scale, which is used in mineralogy. One tool to make this measurement is the sclerometer.
10. In materials science, creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods and generally increases as they near their melting point.

In materials science, fatigue is the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle, typically producing striations on some parts of the fracture surface. The crack will continue to grow until it reaches a critical size, which occurs when the stress intensity factor of the crack exceeds the fracture toughness of the material, producing rapid propagation and typically complete fracture of the structure.

1.6 SUMMARY

- Some external system of forces act on a body, it undergoes some deformation. The deformation increases as the forces increase. If a material regains its original position on the removal of the external forces, it is called an elastic material.
- The physical reasons for elastic behaviour can be quite different for different materials. In metals, the atomic lattice changes size and shape when forces are applied (energy is added to the system). When forces are removed, the lattice goes back to the original lower energy state.
- There are various elastic moduli, such as Young's modulus, the shear modulus, and the bulk modulus, all of which are measures of the inherent elastic properties of a material as a resistance to deformation under an applied load. The various moduli apply to different kinds of deformation.
- The elasticity of materials is described by a stress–strain curve, which shows the relation between stress (the average restorative internal force per unit area) and strain (the relative deformation). The curve is generally nonlinear, but it can (by use of a Taylor series) be approximated as linear for sufficiently small deformations (in which higher-order terms are negligible).
- For small deformations, most elastic materials such as springs exhibit linear elasticity and can be described by a linear relation between the stress and strain. This relationship is known as Hooke's law.
- Cauchy elasticity includes non-conservative 'Non-Hyper elastic' models (in which work of deformation is path dependent) as well as conservative 'Hyper Elastic Material' models (for which stress can be derived from a scalar 'Elastic Potential' function).
- The inelastic behaviour of material, to cross-section, to critical region, and, finally, to the entire structure. In earthquake engineering, inelastic response is probable, and survivability of organisations depends on the ability of the organisation to weather several cycles of fully reversed inelastic deformation without extreme loss of difficulty or strength.

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- Inelastic materials, simply put, are non-elastic materials. They do not show a fixed trend of deformation vs applied force; in fact, they might not deform at all (rigid materials) or the deformation observed is not completely recoverable; on removal of the applied force, the material does not return to its original shape, but to a permanent deformed shape. Such materials are called Plastic materials
- Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials, like water, resist shear flow and strain linearly with time when a stress is applied.
- Viscoelastic materials have elements of both of these properties and, Such as exhibit time-dependent strain. Whereas elasticity is usually the result of bond stretching along crystallographic planes in an ordered solid, viscosity is the result of the diffusion of atoms or molecules inside an amorphous material.
- When the stress is independent of this strain rate, the material exhibits plastic deformation. Many viscoelastic materials exhibit rubber like behaviour explained by the thermodynamic theory of polymer elasticity
- Tensile strength is a measurement of the force required to pull something, such as rope, wire, or a structural beam to the point where it breaks. The tensile strength of a material is the maximum amount of tensile stress that it can take before failure, for example breaking.
- Definition of material toughness is the amount of energy per unit volume that a material can absorb before rupturing. This measure of toughness is different from that used for fracture toughness, which describes load bearing capabilities of materials with flaws. It is also defined as a material's resistance to fracture when stressed.
- Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining the change in length from original. Elongation is expressed as a percentage of the original length. Ultimate elongation is the percentage change in length from original to rupture.
- Under tensile stress, plastic deformation is characterized by a strain hardening region and a necking region and finally, fracture (also called rupture). During strain hardening the material becomes stronger through the movement of atomic dislocations.
- Hardness is a measure of the resistance to localized plastic deformation induced by either mechanical indentation or abrasion. In general, different materials differ in their hardness, for example hard metals such as titanium

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and beryllium are harder than soft metals such as sodium and metallic tin, or wood and common plastics

- Indentation hardness measures the resistance of a sample to material deformation due to a constant compression load from a sharp object. Tests for indentation hardness are primarily used in engineering and metallurgy fields.
- Scratch hardness is the measure of how resistant a sample is to fracture or permanent plastic deformation due to friction from a sharp object. The principle is that an object made of a harder material will scratch an object made of a softer material when testing coatings, scratch hardness refers to the force necessary to cut through the film to the substrate. The most common test is Mohs scale, which is used in mineralogy.
- In materials science, creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods and generally increases as they near their melting point.
- In materials science, fatigue is the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle, typically producing striations on some parts of the fracture surface. The crack will continue to grow until it reaches a critical size, which occurs when the stress intensity factor of the crack exceeds the fracture toughness of the material, producing rapid propagation and typically complete fracture of the structure.

1.7 KEY WORDS

- **Elastic material:** Some external system of forces act on a body, it undergoes some deformation. The deformation increases as the forces increase. If a material regains its original position on the removal of the external forces, it is called an elastic material.
- **Tensile strength:** Tensile strength is a measurement of the force required to pull something, such as rope, wire, or a structural beam to the point where it breaks.
- **Elongation:** Elongation is measured by applying tensile force, or stretching the material in the same manner as described previously, and determining the change in length from original. Elongation is expressed as a percentage

of the original length. Ultimate elongation is the percentage change in length from original to rupture.

- **Creep:** In materials science, creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses.
- **Fatigue:** In materials science, fatigue is the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle, typically producing striations on some parts of the fracture surface.

1.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What is the elastic behavior of materials?
2. Explain about the viscoelastic and inelastic.
3. Define the term tensile strength.
4. How the toughness is measured?
5. Write short note of elongation.
6. What is the plastic deformation?
7. What do you understand by hardness?
8. Differentiate between creep and fatigue.

Long-Answer Questions

1. Briefly discuss the elastic behavior of materials. Give appropriate examples.
2. Analyses the inelastic and viscoelastic behavior.
3. Elaborate on the tensile strength
4. Discuss about the toughness.
5. Explain about the elongation.
6. Explain about the plastic deformation giving examples.
7. Elaborate on the hardness. Discuss about its different features.
8. Explain briefly about the creep and fatigue giving examples.

1.9 FURTHER READINGS

NOTES

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UNIT 2 POLYMERS

NOTES

Structure

2.0 INTRODUCTION

Polymer physics is the field of physics that studies polymers, their fluctuations, mechanical properties, as well as the kinetics of reactions involving degradation and polymerisation of polymers and monomers respectively.

While it focuses on the perspective of condensed matter physics, polymer physics is originally a branch of statistical physics. Polymer physics and polymer chemistry are also related with the field of polymer science, where this is considered the applicative part of polymers. Polymers are large molecules and thus are very complicated for solving using a deterministic method. Yet, statistical approaches can yield results and are often pertinent, since large polymers (i.e., polymers with many monomers) are describable efficiently in the thermodynamic limit of infinitely many monomers (although the actual size is clearly finite).

Thermal fluctuations continuously affect the shape of polymers in liquid solutions, and modelling their effect requires using principles from statistical mechanics and dynamics. As a corollary, temperature strongly affects the physical behaviour of polymers in solution, causing phase transitions, melts, and so on. The statistical approach for polymer physics is based on an analogy between a polymer and either a Brownian motion, or other type of a random walk, the self-avoiding walk. The simplest possible polymer model is presented by the ideal chain, corresponding to a simple random walk. Experimental approaches for characterizing polymers are also common, using polymer characterisation methods, such as size exclusion chromatography, viscometry, dynamic light scattering, and Automatic Continuous Online Monitoring of Polymerisation Reactions (ACOMP) for determining the chemical, physical, and material properties of polymers. These experimental methods also helped the mathematical modelling of polymers and even for a better understanding of the properties of polymers.

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The first modern example of polymer science is Henri Braconnot's work in the 1830s. Henri, along with Christian Schönbein and others, developed derivatives of the natural polymer cellulose, producing new, semi-synthetic materials, such as celluloid and cellulose acetate. The term "polymer" was coined in 1833 by Jöns Jakob Berzelius, though Berzelius did little that would be considered polymer science in the modern sense. In the 1840s, Friedrich Ludersdorf and Nathaniel Hayward independently discovered that adding sulfur to raw natural rubber (polyisoprene) helped prevent the material from becoming sticky. In 1844 Charles Goodyear received a U.S. patent for vulcanizing natural rubber with sulfur and heat. Thomas Hancock had received a patent for the same process in the UK the year before. This process strengthened natural rubber and prevented it from melting with heat without losing flexibility. This made practical products such as waterproofed articles possible. It also facilitated practical manufacture of such rubberized materials. Vulcanized rubber represents the first commercially successful product of polymer research. In 1884 Hilaire de Chardonnet started the first artificial fiber plant based on regenerated cellulose, or viscose rayon, as a substitute for silk, but it was very flammable. In 1907 Leo Baekeland invented the first synthetic plastic, a thermosetting phenol–formaldehyde resin called Bakelite. Despite significant advances in polymer synthesis, the molecular nature of polymers was not understood until the work of Hermann Staudinger in 1922. Prior to Staudinger's work, polymers were understood in terms of the association theory or aggregate theory, which originated with Thomas Graham in 1861. Graham proposed that cellulose and other polymers were colloids, aggregates of molecules having small molecular mass connected by an unknown intermolecular force. Hermann Staudinger was the first to propose that polymers consisted of long chains of atoms held together by covalent bonds. It took over a decade for Staudinger's work to gain wide acceptance in the scientific community, work for which he was awarded the Nobel Prize in 1953.

In this unit, you will study about the Polymers, structure and properties, addition and condensation, polymerisation, type of polymers.

2.1 OBJECTIVES

After going through this unit, you will be able to:

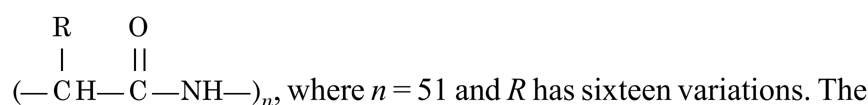
- Illustrate of polymers
- Analyse structure and properties of polymers
- Discuss about the addition and condensation of polymers
- Explain about the polymerisation
- Describe the type of polymers

2.2 POLYMERS

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Polymers are one of the most important products, which find an important place in every walk of modern civilisation. The term polymer (Greak word: *poly* + *meros*, means, many parts) denotes a molecule produced by the repetition of some simpler unit, called the mer or the monomer.

The term *macromolecule* (big molecule) is also often used to cover the large molecule of complex structure. A naturally occurring macromolecule is insulin, a protein hormone, which occurs in the pancreas, and is best known agent to lower blood sugar in diabetic patients. It has the repeating units with amide linkages, i.e.,



, where $n = 51$ and R has sixteen variations. The science of macromolecules is divided between biological and non-biological materials, each having vital importance in our daily life. Biological polymers, i.e., proteins, nucleic acids (DNA, RNA), starch, cellulose and enzymes are complex macro molecules which form the very foundation of life and intelligence and provide much of the food for the existance of man. This unit however, is concerned mainly with the chemistry of some polymers. These are primarily the synthetic materials used for plastics, fibers, and elastomers and a few naturally occurring polymers, such as rubber, wool and cellulose. The polymers are truly indispensible to mankind, as they are used to meet the basic needs-clothing, shelter, communication, and transportation, as well as to the conveniences of modern living.

The name of a polymer is usually derived from the name of the monomer (repeat unit) by prefixing the word poly to it. To illustrate the polymerisation product of ethylene is known as polyethylene and that of sytrene is called polystyrene. The number of repeating units in the chain is called the Degree of Polymerisation (DP) and specifies the length of the chain. Degree of polymerization is denoted by the letter n or P. The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the degree of polymerisation, i.e.,

$$M_{\text{poly}} = n \times M_m$$

or

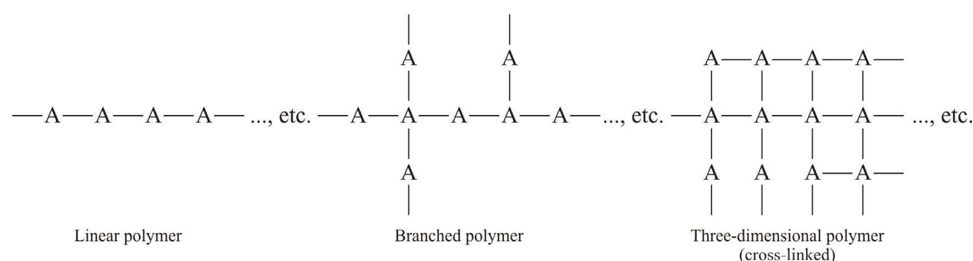
$$n \text{ (Degree of polymerisation)} = \frac{M_{\text{poly}} \text{ (mol. wt. of polymer)}}{M_m \text{ (mol. wt. of repeat unit)}}$$

The degree of polymerisation may vary over a wide range, i.e., from a few units to 10,000 and even more. Polymers with high P are called high polymers and are mostly useful for plastics, rubbers or fibres, etc., while those with low P are known as oligomers.

2.3 STRUCTURE AND PROPERTIES

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A polymer may consist of monomers of identical or of different chemical structure. If it has identical units then it is known as homopolymer, whereas a polymer containing several types of monomeric units in its chain is known as copolymer, or mixed polymer. In some cases the repetition is linear and a chain is built up from its links. However, in some cases the chains are branched or interconnected, to form three dimensional structures.



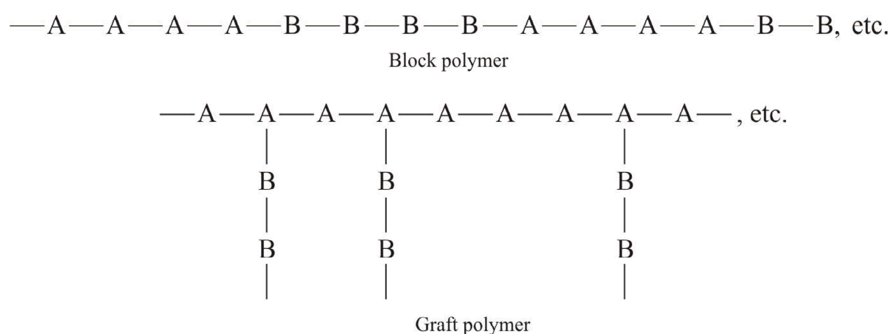
Copolymers may also be linear, branched or three-dimensional. The monomer residues, in co-polymer molecules may be arranged in the chain regularly or at random, according to the law of chance. Copolymers of the former group are called regular-copolymers and those of latter type, statistical or irregular copolymers.

Copolymers with long sequence of two monomers can have two arrangements of long chains:

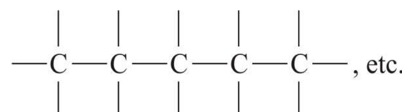
1. linear copolymers in which the units of each type form fairly continuous sequence (blocks) is known as block copolymers.
2. Branched copolymer, with monomer of one kind grafted into a backbone of the second monomer type is termed as graft copolymer.

According to the structure of main chain, all polymers are classified into homochain and heterochain polymers. Homochain polymers contain the chains composed of atoms of the same element, e.g., carbon, sulphur phosphorus, etc.

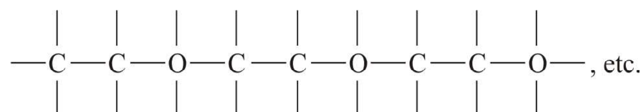
In heterochain polymers, the main chain is made up of atoms of different species, e.g.,



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Carbon-chain polymer



Heterochain polymer

On the basis of chemical composition, the polymers can also be classified as:

1. **Organic polymers:** Organic polymers include compounds containing carbon hydrogen, oxygen nitrogen, sulphur and halogen atoms. Oxygen, nitrogen or sulphur may also be present in the backbone chain.
2. **Elemento-organic (hetero-organic) polymers:** These include the following classes:
   (*i*) Compounds containing carbon atoms and hetero atoms (except for nitrogen, sulphur and oxygen atoms) in their chains.
   (*ii*) Compounds with inorganic chains if they contain side groups with carbon atoms connected directly to the chain.
   (*iii*) Compounds having carbon atoms in the main chain and hetero-atoms (except for nitrogen, sulphur, oxygen and halogen atoms) in side groups connected directly to the carbon atoms of the chain. For example, polysiloxanes, polytitanoxanes, etc.
3. **Inorganic polymers:** These include polymers containing no carbon atoms. Their are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between their chains. Polysilanes, polygermanes, polysilicic acid, polyphosphates, polyarsenates, etc., are examples of inorganic polymers.

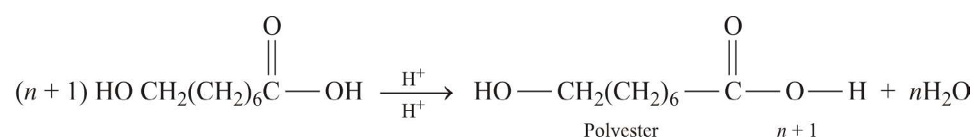
2.4 POLYMERISATION PROCESSES

The processes of polymerisation were classified by the W H Carothers (1926) into two groups, i.e., *condensation* and *addition* polymerizations. In 1953, Flory amended Carother's original distinction between addition and condensation polymeridation. He laid special emphasis on the mechanisms by which the two types of polymerisation proceed. It was observed that condensation polymerisation was preceded by the stepwise intermolecular condensation of reactive groups and the addition polymerisation resulted from chain reactions involving some sort of active centres.

Thus, the two classes of polymerzation are:

Condensation Polymerisation

This is entirely analogous to condensation in low molecular weight compounds. For the formation of condensation polymer there is union between two polyfunctional molecules to produce the large polyfunctional molecule. The process involves the elimination of a small molecule, such as water, ammonia, etc. The reaction continues until almost all of the reagents is used up. Since there is an equilibrium between reactants and products, the rate of conversion can be controlled by the rate of removal of one of the products. A good example is, esterification, where water is eliminated between an acid and an alcohol.



Here, the rate of conversion can be controlled by the rate of removal of water.

Addition or Chain-reaction Polymerization

This type of polymerization involves chain reactions. The chain carrier in such reactions may be an ion or a reactive substance with one unpaired electron called a free radical. Chain polymerisation is characteristic of compounds with multiple bonds, e.g., ethylene CH_2=CH_2. isobutylene $(CH_3)_2$ C=CH_2 and vinyl chloride CH_2=CHCl, or of unstable rings containing heteroatoms, e.g., ethylene oxide CH_2 — CH_2 (bridged by O). Depending upon the active centre, which may be a free radical or an ion, the reaction is one of radical or ionic polymerization, respectively. A free radical is produced by the decomposition of an initiator. The free radical then attacks to open the double bond of a vinyl monomer or ring or a cyclic compound and adds to it, with an electron remaining unpaired. Within a very short span of time (usually a few seconds or less) many more monomers add successively to form a long chain with active centers. Finally, chain termination results from saturation of the macro radical and may occur by the combination of free radicals, disproportionation of chain transfer.

With few exceptions, chain-reaction polymerization results in the formation of homochain polymers, where as step-reaction polymerization produces heterochain polymers. Polymerizations are classified without regard to loss of a small molecule (e.g., polyurethanes are formed by step-reaction polymerization or type of interunit linkage (e.g., phenol-formaldehyde resins results from stepwise polymerization even though they lack interunit functional groups). In case the differentiation is required on the basis of mechanism, the terms *step-reaction* and *chain-reaction* are used; but to avoid confusion, the common terms *condensation* and *addition* are permissible.

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Properties

Polymeric materials possess a very wide range of physical properties, they are hard or soft or rubber-like, brittle or tough and malleable and non-malleable. These properties depends on the molecular structure of the polymer. The physical properties depend to a great extent on whether the polymer is (*i*) completely amorphous or (*ii*) partly crystalline. In an amorphous polymer the molecular chains are all tangled up in a disordered manner. The long chain polymers generally exist in the amorphous state this is because the long chains mostly exist in the random coiled configuration, the solid is thus clastic. However, due to the presence of some crystallinity the polymeric material is stiffer. Depending on the temperature of the amorphous polymer may be glassy or leathery.

Group OH Cl CN NO_2 H NH_2 CH_3

Most polymers are in the glassy state which is like that of a supercooled liquid. On raising the temperature there is a transition at the glass-transition temperature from the glassy to the leathery state. Below the glass-transition temperature of a polymeric substance can be raised by vulcanisation due to cross-linkages.

The mechanical properties of polymers are profoundly dependent on the stereo-regularity of their chains. Polymers of monomers like styrene have symmetric carbon atoms. There are two types of stereoregular vinyl polymers, isotactic and syndictactic depending on whether successive pseudoasymmetric carbon atoms have the same or opposite enantiomorphic configuration. Some polymers contain regions in which the chains are arranged in an orderly three dimensional array. These crystalline regions typically have dimensions of the order of 10 mm and they have an important influence on the physical properties of the polymer. The extent of crystallinity of the polymer is increased as it is stretched. This because on stretching the chains are drawn together thus reducing the random thermal motion.

2.5 POLYMER TYPE

A polymer (Greek poly-, 'Many' + -mer, 'Part') is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits. Due to their broad spectrum of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics, such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass, relative to small molecule compounds, produces unique physical properties including toughness, high elasticity, viscoelasticity, and a tendency to form amorphous and semi crystalline structures rather than crystals.

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The term - 'Polymer' derives from the Greek word polus, meaning 'Many, Much' and meros, meaning 'Part'), and refers to large molecules whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by Jöns Jacob Berzelius, though with a definition distinct from the modern IUPAC definition. The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis.

Polymers are studied in the fields of polymer science (which includes polymer chemistry and polymer physics), biophysics and materials science and engineering. Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science. An emerging important area now focuses on supramolecular polymers formed by non-covalent links.

Polyisoprene of latex rubber is an example of a natural polymer, and the polystyrene of styrofoam is an example of a synthetic polymer. In biological contexts, essentially all biological macromolecules—i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides—are purely polymeric, or are composed in large part of polymeric components.

Polymers are of two types: naturally occurring and synthetic or man-made.

Natural

Natural polymeric materials, such as hemp, shellac, amber, wool, silk, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

Synthetic

The list of synthetic polymers, roughly in order of worldwide demand, includes polyethylene, polypropylene, polystyrene, polyvinyl chloride, synthetic rubber, phenol formaldehyde resin (or Bakelite), neoprene, nylon, polyacrylonitrile, PVB, silicone, and many more. More than 330 million tons of these polymers are made every year (2015).

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene ('polythene' in British English), whose repeating unit is based on ethylene monomer. Many other structures do exist; for example, elements, such as silicon form familiar materials, such as silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

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Polymers have been essential components of commodities since the early days of humankind. The use of wool (keratin), cotton and linen fibres (cellulose) for garments, paper reed (cellulose) for paper are just a few examples of how our ancestors exploited polymer-containing raw materials to obtain artefacts. The latex sap of "cautchouc" trees (natural rubber) reached Europe in the 16th century from South America long after the Olmec, Maya and Aztec had started using it as a material to make balls, waterproof textiles and containers.

The chemical manipulation of polymers dates back to the 19th century, although at the time the nature of these species was not understood. The behaviour of polymers was initially rationalised according to the theory proposed by Thomas Graham which considered them as colloidal aggregates of small molecules held together by unknown forces.

Notwithstanding the lack of theoretical knowledge, the potential of polymers to provide innovative, accessible and cheap materials was immediately grasped. The work carried out by Braconnot, Parkes, Ludersdorf, Hayard and many others on the modification of natural polymers determined many significant advances in the field. Their contributions led to the discovery of materials such as celluloid, galalith, parkesine, rayon, and vulcanised rubber and, later, Bakelite: all materials that quickly entered industrial manufacturing processes and reached households as garments components (e.g., fabrics, buttons), crockery and decorative items.

In 1920, Hermann Staudinger published his seminal work 'Über Polymerisation' in which he proposed that polymers were in fact long chains of atoms linked by covalent bonds. His work was debated at length, but eventually it was accepted by the scientific community. Because of this work, Staudinger was awarded the Nobel Prize in 1953.

After the 1930s polymers entered a golden age during which new types were discovered and quickly given commercial applications, replacing naturally-sourced materials. This development was fuelled by an industrial sector with a strong economical drive and it was supported by a wide academic community that contributed with innovative synthesis of monomers from cheaper raw materials, more efficient polymerisation processes, improved techniques for polymer characterisation and advanced theoretical understanding of polymers.

Check Your Progress

1. Define the term polymers.
2. What are the biological polymers?
3. Write the names of compound in organic polymers.
4. Explain about the inorganic polymers.
5. Write the process of polymerisation.
6. Explain the free radical.
7. What are natural polymers?

2.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

NOTES

1. Polymers are one of the most important products, which find an important place in every walk of modern civilisation. The term polymer (Greak word: poly + meros, means, many parts) denotes a molecule produced by the repetition of some simpler unit, called the mer or the monomer.
2. Biological polymers, i.e., proteins, nucleic acids (DNA, RNA), starch, cellulose and enzymes are complex macro molecules which form the very foundation of life and intelligence and provide much of the food for the existance of man.
3. Organic polymers: Organic polymers include compounds containing carbon hydrogen, oxygen nitrogen, sulphur and halogen atoms. Oxygen, nitrogen or sulphur may also be present in the backbone chain.
4. Inorganic polymers: These include polymers containing no carbon atoms. Their are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between their chains. Polysilanes, polygermanes, polysilicic acid, polyphosphates, polyarsenates, etc., are examples of inorganic polymers.
5. The processes of polymerisation were classified by the W H Carothers (1926) into two groups, i.e., condensation and addition polymerizations. In 1953, Flory amended Carother's original distinction between addition and condensation polymeridation.
6. This type of polymerization involves chain reactions. The chain carrier in such reactions may be an ion or a reactive substance with one unpaired electron called a free radical.
7. Natural polymeric materials such as hemp, shellac, amber, wool, silk, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

2.7 SUMMARY

- Polymers are one of the most important products, which find an important place in every walk of modern civilisation. The term polymer (Greak word: poly + meros, means, many parts) denotes a molecule produced by the repetition of some simpler unit, called the mer or the monomer.

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- The term macromolecule (big molecule) is also often used to cover the large molecule of complex structure. A naturally occurring macromolecule is insulin, a protein hormone, which occurs in the pancreas, and is best known agent to lower blood sugar in diabetic patients.
- Science of macromolecules is divided between biological and non-biological materials, each having vital importance in our daily life.
- The polymers are truly indispensable to mankind, as they are used to meet the basic needs-clothing, shelter, communication, and transportation, as well as to the conveniences of modern living
- The name of a polymer is usually derived from the name of the monomer (repeat unit) by prefixing the word poly to it. To illustrate the polymerization product of ethylene is known as polyethylene and that of sytrene is called polystyrene.
- A polymer may consist of monomers of identical or of different chemical structure. If it has identical units then it is known as homopolymer, whereas a polymer containing several types of monomeric units in its chain is known as copolymer, or mixed polymer.
- Copolymers may also be linear, branched or three-dimensional. The monomer residues, in co-polymer molecules may be arranged in the chain regularly or at random, according to the law of chance. Copolymers of the former group are called regular-copolymers and those of latter type, statistical or irregular copolymers.
- Organic polymers include compounds containing carbon hydrogen, oxygen nitrogen, and sulphur and halogen atoms. Oxygen, nitrogen or sulphur may also be present in the backbone chain.
- Compounds having carbon atoms in the main chain and heteroatoms (except for nitrogen, sulphur, oxygen and halogen atoms) in side groups connected directly to the carbon atoms of the chain. For example, polysiloxanes, polytitanoxanes, etc.
- Inorganic polymers containing no carbon atoms. There are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between their chains.
- The processes of polymerisation were classified by the W H Carothers (1926) into two groups, i.e., condensation and addition polymerizations. In 1953, Flory amended Carother's original distinction between addition and condensation polymeridation. He laid special emphasis on the mechanisms by which the two types of polymerisation proceed.
- Condensation polymerisation is entirely analogous to condensation in low molecular weight compounds. For the formation of condensation polymer there is union between two polyfunctional molecules to produce the large polyfunctional molecule.

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- Addition or chain-reaction Polymerisation type of polymerisation involves chain reactions. The chain carrier in such reactions may be an ion or a reactive substance with one unpaired electron called a free radical.
- Chain-reaction polymerisation results in the formation of homochain polymers, whereas step-reaction polymerisation produces heterochain polymers.
- Polymeric materials possess a very wide range of physical properties, they are hard or soft or rubber-like, brittle or tough and malleable and non-malleable. These properties depends on the molecular structure of the polymer.
- Most polymers are in the glassy state which is like that of a supercooled liquid. On raising the temperature there is a transition at the glass-transition temperature from the glassy to the leathery state. Below the glass-transition temperature of a polymeric substance can be raised by vulcanisation due to crosslinkages.
- The mechanical properties of polymers are profoundly dependent on the stereo-regularity of their chains. Polymers of monomers like styrene have symmetric carbon atoms. There are two types of stereoregular vinyl polymers, isotactic and syndictactic depending on whether successive pseudoasymmetric carbon atoms have the same or opposite enantiomorphic configuration.
- Some polymers contain regions in which the chains are arranged in an orderly three dimensional array. These crystalline regions typically have dimensions of the order of 10 mm and they have an important influence on the physical properties of the polymer.
- Polymers are studied in the fields of polymer science (which includes polymer chemistry and polymer physics), biophysics and materials science and engineering. Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science.
- Polyisoprene of latex rubber is an example of a natural polymer, and the polystyrene of styrofoam is an example of a synthetic polymer. In biological contexts, essentially all biological macromolecules , i.e., proteins (polyamides), nucleic acids (polynucleotides).
- Natural polymeric materials such as hemp, shellac, amber, wool, silk, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.
- The list of synthetic polymers, roughly in order of worldwide demand, includes polyethylene, polypropylene, polystyrene, polyvinyl chloride, synthetic rubber, phenol formaldehyde resin (or Bakelite), neoprene, nylon, polyacrylonitrile, PVB, silicone, and many more.

2.8 KEY WORDS

NOTES

- **Organic polymers:** Organic polymers include compounds containing carbon hydrogen, oxygen nitrogen, sulphur and halogen atoms. Oxygen, nitrogen or sulphur may also be present in the backbone chain.
- **Inorganic polymers:** These include polymers containing no carbon atoms. Their are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between their chains. Polysilanes, polygermanes, polysilicic acid, polyphosphates, polyarsenates, etc., are examples of inorganic polymers.
- **Polymerisation:** The processes of polymerisation were classified by the W H Carothers (1926) into two groups, i.e., condensation and addition polymerizations. In 1953, Flory amended Carother's original distinction between addition and condensation polymeridation. He laid special emphasis on the mechanisms by which the two types of polymerisation proceed.
- **Natural polymers:** Natural polymeric materials such as hemp, shellac, amber, wool, silk, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.
- **Synthetic polymers:** The list of synthetic polymers, roughly in order of worldwide demand, includes polyethylene, polypropylene, polystyrene, polyvinyl chloride, synthetic rubber, phenol formaldehyde resin (or Bakelite), neoprene, nylon, polyacrylonitrile, PVB, silicone, and many more.

2.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the term polymer.
2. What is polymerisation? Write the formula and degree of polymerisation.
3. Give the classification of polymers.
4. What is condensation polymerisation?
5. Explain about the addition chain reaction polymerisation.
6. What is He-Ne Laser?
7. Explain the various types of polymers.

Long-Answer Questions

1. Explain briefly about the polymers giving its chemical structure and properties.
2. Elaborate on the addition and condensation of polymers giving examples.

3. Discuss about the polymerisation process.
4. Explain about the structure and properties of polymers.
5. Briefly explain about the different types of polymers giving examples.

NOTES

2.10 FURTHER READINGS

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UNIT 3 APPLICATIONS OF POLYMERS

NOTES

Structure

3.0 INTRODUCTION

The term 'Polymer' derives from the Greek word (polus, meaning 'Many, Much') and (meros, meaning 'Part'), and refers to large molecules whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by Jöns Jacob Berzelius, though with a definition distinct from the modern IUPAC definition. The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis.

Polymers are studied in the fields of polymer science (which includes polymer chemistry and polymer physics), biophysics and materials science and engineering. Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science. An emerging important area now focuses on supramolecular polymers formed by non-covalent links. Polyisoprene of latex rubber is an example of a natural polymer, and the polystyrene of styrofoam is an example of a synthetic polymer. In biological contexts, essentially all biological macromolecules, i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides are purely polymeric or are composed in large part of polymeric components.

Corrosion is a natural process that converts a refined metal into a more chemically stable form, such as oxide, hydroxide, or sulphide. It is the gradual destruction of materials (usually a metal) by chemical and electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling

and preventing corrosion. Passivation refers to the spontaneous formation of an ultrathin film of corrosion products, known as a passive film, on the metals surface that act as a barrier to further oxidation. Some metals are more intrinsically resistant to corrosion than others. There are various ways of protecting metals from corrosion (oxidation) including painting, hot dip galvanising, cathodic protection, and combinations of these.

In this unit, you will study about the applications of polymers, corrosion and oxidation of metal, prevention, corrosion resistance material.

3.1 OBJECTIVES

After going through this unit, you will be able to:

- Elaborate on the important application of polymers
- Understand the significance of corrosion and oxidation of metals
- Explain about the prevention
- Analyse the corrosion resistance material

3.2 APPLICATIONS OF POLYMERS

A polymer (Greek word poly-, 'Many' + -mer, 'Part') is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits. Due to their broad spectrum of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers, such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass, relative to small molecule compounds, produces unique physical properties including toughness, high elasticity, viscoelasticity, and a tendency to form amorphous and semi crystalline structures rather than crystals.

Polymers are studied in the fields of polymer science (which includes polymer chemistry and polymer physics), biophysics and materials science and engineering. Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science. An emerging important area now focuses on supramolecular polymers formed by non-covalent links. Polyisoprene of latex rubber is an example of a natural polymer, and the polystyrene of styrofoam is an example of a synthetic polymer. In biological contexts, essentially all biological macromolecules, i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides are purely polymeric, or are composed in large part of polymeric components.

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Nowadays, synthetic polymers are used in almost all walks of life. Modern society would look very different without them. The spreading of polymer use is connected to their unique properties: low density, low cost, good thermal/electrical insulation properties, high resistance to corrosion, low-energy demanding polymer manufacture and facile processing into final products. For a given application, the properties of a polymer can be tuned or enhanced by combination with other materials, as in composites. Their application allows to save energy (lighter cars and planes, thermally insulated buildings), protect food and drinking water (packaging), save land and reduce use of fertilizers (synthetic fibres), preserve other materials (coatings), protect and save life's (hygiene, medical applications). A representative, non-exhaustive list of applications is given below.

- **Clothing, sportswear and accessories:** polyester and Polyvinyl Chloride (PVC) clothing, spandex, sport shoes, wetsuits, footballs and billiard balls, skis and snowboards, rackets, parachutes, sails, tents and shelters.
- **Electronic and photonic technologies:** Organic Field Effect Transistors (OFET), Light Emitting Diodes (LED) and solar cells, television components, Compact Discs (CD), photoresists, holography.
- **Packaging and containers:** films, bottles, food packaging, barrels.
- **Insulation:** electrical and thermal insulation, spray foams.
- **Construction and structural applications:** garden furniture, PVC windows, flooring, sealing, pipes.
- **Paints:** paints, glues and lubricants: varnish, adhesives, dispersants, anti-graffiti coatings, antifouling coatings, non-stick surfaces, lubricants.
- **Car parts:** tires, bumpers, windshields, windscreen wipers, fuel tanks, car seats.
- **Household items:** buckets, kitchenware, toys (e.g., construction sets and Rubik's cube).
- **Medical applications:** blood bag, syringes, rubber gloves, surgical suture, contact lenses, prosthesis, controlled drug delivery and release, matrices for cell growth.
- **Personal hygiene and healthcare:** diapers using superabsorbent polymers, toothbrushes, cosmetics, shampoo, condoms.
- **Security:** personal protective equipment, bulletproof vests, space suits, ropes.
- **Separation technologies:** synthetic membranes, fuel cell membranes, filtration, ion-exchange resins.
- **Money:** polymer banknotes and payment cards.
- **3D Printing**.

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3.3 CORROSION AND OXIDATION OF METALS

Corrosion is a natural process that converts a refined metal into a more chemically stable form, such as oxide,, hydroxide, or sulphide. It is the gradual destruction of materials (usually a metal) by chemical and electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulphates. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces Oxide(O) or Salt(S) of the original metal and results in a distinctive orange colouration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term 'Degradation' is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases.

Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly

Corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. During corrosion at a particular spot on the surface of the object made of iron, oxidation takes place and that spot behaves as an anode. The electrons released at this anodic spot move through the metal and go to another spot on the metal and reduce oxygen at that spot in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water in moist air condition of atmosphere. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as a cathode.

Galvanic Corrosion

Galvanic corrosion of an aluminium plate occurred when the plate was connected to a mild steel structural support.

Galvanic corrosion occurs when two different metals have physical or electrical contact with each other and are immersed in a common electrolyte, or when the same metal is exposed to electrolyte with different concentrations. In a galvanic couple, the more active metal (the anode) corrodes at an accelerated

rate and the more noble metal (the cathode) corrodes at a slower rate. When immersed separately, each metal corrodes at its own rate. What type of metal(s) to use is readily determined by following the galvanic series? For example, zinc is often used as a sacrificial anode for steel structures..

Galvanic corrosion is of major interest to the marine industry and also anywhere water (containing salts) contacts pipes or metal structures.

Factor, such as relative size of anode, types of metal, and operating conditions (temperature, humidity, salinity, etc.) affect galvanic corrosion. The surface area ratio of the anode and cathode directly affects the corrosion rates of the materials. Galvanic corrosion is often prevented by the use of sacrificial anodes.

Galvanic Series

In any given environment (one standard medium is aerated, room-temperature seawater), one metal will be either more noble or more active than others, based on how strongly its ions are bound to the surface. Two metals in electrical contact share the same electrons, so that the 'tug-of-war' at each surface is analogous to competition for free electrons between the two materials. Using the electrolyte as a host for the flow of ions in the same direction, the noble metal will take electrons from the active one. The resulting mass flow or electric current can be measured to establish a hierarchy of materials in the medium of interest. This hierarchy is called a galvanic series and is useful in predicting and understanding corrosion.

Resistance to Corrosion

Some metals are more intrinsically resistant to corrosion than others (for some examples, see galvanic series). There are various ways of protecting metals from corrosion (oxidation) including painting, hot dip galvanising, cathodic protection, and combinations of these.

Intrinsic Chemistry



Gold nuggets do not naturally corrode, even on a geological time scale.

The materials most resistant to corrosion are those for which corrosion is thermodynamically unfavourable. Any corrosion products of gold or platinum tend to decompose spontaneously into pure metal, which is why these elements can be found in metallic form on Earth and have long been valued. More common 'Base' metals can only be protected by more temporary means.

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Some metals have naturally slow reaction kinetics, even though their corrosion is thermodynamically favourable. These include such metals as zinc, magnesium, and cadmium. While corrosion of these metals is continuous and ongoing, it happens at an acceptably slow rate. An extreme example is graphite, which releases large amounts of energy upon oxidation, but has such slow kinetics that it is effectively immune to electrochemical corrosion under normal conditions.

3.4 PREVENTION

Corrosion Prevention Methods

We recognise the significance of corrosion prevention. Rust and other corrosion forms can lead to safety issues and ruin the integrity of your apparatus and materials. Even routine maintenance to remove and repair corrosion can drive up costs. Fortunately, there are a variety of measures you can take to minimize corrosion. Here we all highlight four of these methods based on cost and effectiveness.

1. Barrier Coatings

One of the informal and inexpensive ways to prevent corrosion is to use barrier coatings like paint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film. Plastic and waxes are often sprayed onto metal surfaces. Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds. Today's paint systems are actually a combination of different paint layers that serve different functions. The primer coat acts as an inhibitor, the intermediate coat adds to the paint's overall thickness, and the finish coat provides resistance to the environmental factors.

The biggest drawback with coatings is that they often need to be stripped and reapplied. Coatings that aren't applied properly can quickly fail and lead to increased levels of corrosion. Coatings may also contain volatile organic compounds, which can make them vulnerable to corrosion.

2. Hot-Dip Galvanization

This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection. The process has been around for more than 250 years and has been used for corrosion protection of things like artistic sculptures and playground equipment. Compared to other corrosion prevention methods, galvanization is known for lower initial costs, sustainability, and versatility.

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Unfortunately, galvanisation cannot be done on-site, meaning companies have to pull equipment out of work to be treated. Some equipment may simply be too large for the process, forcing companies to abandon the idea altogether. In addition, if the process isn't done properly, the zinc can chip or peel. And high exposure to environmental elements can speed up the process of zinc wear, leading to increased maintenance check-ups. Lastly, the zinc fumes that release from the galvanising process are toxic.

3. Alloyed Steel (Stainless)

Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product. Corrosion-resistant nickel, for example, combined with oxidation-resistant chromium results in an alloy that can be used in oxidized and reduced chemical environments. Different alloys provide resistance to different conditions, giving companies greater flexibility.

Despite its effectiveness, alloyed steel is very expensive. Companies with limited financial resources will likely have to turn to other methods. Monitoring surface conditions are critical, as cracks or scratches can result in an increase of corrosion. Companies also need to make sure the agents used in maintenance do not include corrosion properties.

4. Cathodic Protection

Cathodic protection protects against galvanic corrosion, which occurs when two different metals are put together and exposed to a corrosive electrolyte. To prevent this, the active sites on the metal surface need to be converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminium, magnesium, or zinc.

While cathodic protection is highly effective, anodes need to be checked often which can drive up costs of maintenance. They also increase the weight on the attached structure and are not always effective in high-resistivity environments. Finally, anodes lead to increased water flow on ships and other subaquatic apparatus.

3.5 CORROSION RESISTANCE MATERIAL

Resistance to Corrosion

Some metals are more intrinsically resistant to corrosion than others (for some examples, see galvanic series). There are various ways of protecting metals from corrosion (oxidation) including painting, hot dip galvanising, cathodic protection, and combinations of these.



Gold nuggets do not naturally corrode, even on a geological time scale.

The materials most resistant to corrosion are those for which corrosion is thermodynamically unfavourable. Any corrosion products of gold or platinum tend to decompose spontaneously into pure metal, which is why these elements can be found in metallic form on Earth and have long been valued. More common "base" metals can only be protected by more temporary means.

Some metals have naturally slow reaction kinetics, even though their corrosion is thermodynamically favourable. These include such metals as zinc, magnesium, and cadmium. While corrosion of these metals is continuous and ongoing, it happens at an acceptably slow

Rate. An extreme example is graphite, which releases large amounts of energy upon oxidation, but has such slow kinetics that it is effectively immune to electrochemical corrosion under normal conditions.

Passivation

Passivation refers to the spontaneous formation of an ultrathin film of corrosion products, known as a passive film, on the metals surface that act as a barrier to further oxidation. The chemical composition and microstructure of a passive film are different from the underlying metal. Typical passive film thickness on aluminium, stainless steels, and alloys is within 10 nanometres. The passive film is different from oxide layers that are formed upon heating and are in the micrometre thickness range – the passive film recovers if removed or damaged whereas the oxide layer does not. Passivation in natural environments such as air, water and soil at moderate pH is seen in such materials as aluminium, stainless steel, titanium, and silicon.

Passivation is primarily determined by metallurgical and environmental factors. The effect of pH is summarized using Pourbaix diagrams, but many other factors are influential. Some conditions that inhibit passivation include high pH for aluminium and zinc, low pH or the presence of chloride ions for stainless steel, high temperature for titanium (in which case the oxide dissolves into the metal, rather than the electrolyte) and fluoride ions for silicon. On the other hand, unusual conditions may result in passivation of materials that are normally unprotected, as the alkaline environment of concrete does for steel rebar. Exposure to a liquid metal such as mercury or hot solder can often circumvent passivation mechanisms.

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Check Your Progress

1. Define the term polymer.
2. Explain about the corrosion of metals.
3. Elaborate on the oxidation of metals.
4. What do you understand by the prevention?
5. What is the corrosion resistance materials?

3.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. A polymer (Greek word poly-, 'Many' + -mer, 'Part') is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits.
2. Corrosion is a natural process that converts a refined metal into a more chemically stable form such as oxide, hydroxide, or sulphide. It is the gradual destruction of materials (usually a metal) by chemical and electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.
3. Electrochemical oxidation of metal in reaction with an oxidant, such as oxygen or sulphates. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal and results in a distinctive orange colouration
4. We recognise the significance of corrosion prevention. Rust and other corrosion forms can lead to safety issues and ruin the integrity of your apparatus and materials. Even routine maintenance to remove and repair corrosion can drive up costs.
5. Some metals are more intrinsically resistant to corrosion than others (for some examples, see galvanic series). There are various ways of protecting metals from corrosion (oxidation) including painting, hot dip galvanizing, cathodic protection, and combinations of these.

3.7 SUMMARY

- A polymer (Greek word poly-, 'Many' + -mer, 'Part') is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits.
- Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function.

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- Polymers are studied in the fields of polymer science (which includes polymer chemistry and polymer physics), biophysics and materials science and engineering. Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science.
- An emerging important area now focuses on supramolecular polymers formed by non-covalent links.
- Polyisoprene of latex rubber is an example of a natural polymer, and the polystyrene of styrofoam is an example of a synthetic polymer.
- In biological contexts, essentially all biological macromolecules, i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides are purely polymeric, or are composed in large part of polymeric components.
- Synthetic polymers are used in almost all walks of life. Modern of Polymers society would look very different without them. The spreading of polymer use is connected to their unique properties: low density, low cost, good thermal/electrical insulation properties, and high resistance to corrosion, low-energy demanding polymer manufacture and facile processing into final products.
- Corrosion is a natural process that converts a refined metal into a more chemically stable form such as oxide, hydroxide, or sulphide. It is the gradual destruction of materials (usually a metal) by chemical and electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.
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- The materials most resistant to corrosion are those for which corrosion is thermodynamically unfavourable. Any corrosion products of gold or platinum

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tend to decompose spontaneously into pure metal, which is why these elements can be found in metallic form on Earth and have long been valued.

- We recognise the significance of corrosion prevention. Rust and other corrosion forms can lead to safety issues and ruin the integrity of your apparatus and materials. Even routine maintenance to remove and repair corrosion can drive up costs.
- Informal and inexpensive ways to prevent corrosion is to use barrier coatings like paint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film.
- Hot-Dip galvanisation corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection.
- Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product.
- Some metals are more intrinsically resistant to corrosion than others (for some examples, see galvanic series). There are various ways of protecting metals from corrosion (oxidation) including painting, hot dip galvanizing, cathodic protection, and combinations of these.
- Passivation refers to the spontaneous formation of an ultrathin film of corrosion products, known as a passive film, on the metals surface that act as a barrier to further oxidation. The chemical composition and microstructure of a passive film are different from the underlying metal.

3.8 KEY WORDS

- **Polymers:** A polymer (Greek word poly-, 'Many' + -mer, 'Part') is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits.
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- **Galvanic corrosion:** Galvanic corrosion occurs when two different metals have physical or electrical contact with each other and are immersed in a common electrolyte, or when the same metal is exposed to electrolyte with different concentrations.
- **Hot-Dip galvanisation:** This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection.

- **Resistance to corrosion:** Some metals are more intrinsically resistant to corrosion than others (for some examples, see galvanic series). There are various ways of protecting metals from corrosion (oxidation) including painting, hot dip galvanizing, cathodic protection, and combinations of these.

3.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the importance of polymers.
2. Explain the important applications of polymers.
3. Define about the corrosion and oxidation of metals.
4. Elaborate on the barrier coatings.
5. What are the corrosion resistance materials?

Long-Answer Questions

1. Describe briefly the applications of polymers with the help of examples.
2. Explain about the corrosion and oxidation of metals giving appropriate examples.
3. Explain the significance of prevention.
4. Discuss briefly the concept of the corrosion resistance materials giving appropriate examples.

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BLOCK - II

THIN FILMS

NOTES

UNIT 4 VACUUM PUMPS

Structure

4.0 INTRODUCTION

A vacuum pump is a device that draws gas molecules from a sealed volume in order to leave behind a partial vacuum. The job of a vacuum pump is to generate a relative vacuum within a capacity. The first vacuum pump was invented in 1650 by Otto von Guericke, and was preceded by the suction pump, which dates to antiquity.

A vacuum pump is a device that is used to creating, improving or maintaining a vacuum in an isolated vessel (an environment in which the pressure is below the atmospheric pressure). Vacuum pump works same as compressors, it runs with the inlet connected to the system where vacuum is to be created and maintained the outlet open to atmosphere. Generally, compressors and vacuum pumps are similar machines. Selection of pump should be based on the range of vacuum produced, air removal rate, leak in the rate, and power needed.

The predecessor to the vacuum pump was the suction pump. Dual-action suction pumps were found in the city of Pompeii. Arabic engineer Al-Jazari later described dual-action suction pumps as part of water-raising machines in the 13th century. He also said that a suction pump was used in siphons to discharge Greek fire. The suction pump later appeared in medieval Europe from the 15th century. The early 20th century saw the invention of many types of vacuum pump, including the molecular drag pump, the diffusion pump, and the turbo molecular pump.

The vacuum pump has a rotor and a stator. Stator houses a cylindrical rotor, it has two radially machined slots opposite to each other. Two spring-loaded

vanes are put in these slots which tightly rub the stator causing when it rotates. A kinetic vacuum pump is a pump in which momentum is transferred to the gas or the gas is transferred continuously from the inlet to the outlet. Kinetic transfer pumps are used as high-speed blades or introduced vapour to direct gas towards the outlet, working on the principle of momentum transfer. Transfer of gas is obtained by a series of high-velocity vapour jets (normally oil vapour is used) coming out from an assembly within the pump body. Turbo molecular works on the principle of momentum transfer. With a rapidly rotating rotor, the gas molecules' initially nondirected thermal motion is converted to a directed motion. Hence, the pumping is obtained by directing the gas molecules from the inlet flange to the burst port where a backing pump has already been connected.

In this unit, you will study about the kinetic theory of gases, gas transport and pumping, vacuum pump, rotary diffusion and turbo molecular pumps, pirani and penning gauges.

4.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss about the kinetic theory of gases
- Explain the gas transport and pumping
- Introduces of vacuum pumps
- Understand the rotary, diffusion and turbo molecular pumps
- Illustrate the pirani and penning gauges

4.2 KINETIC THEORY OF GASES

The kinetic theory of gases is a simple, historically significant model of the thermodynamic behaviour of gases, With which many **principle** concepts of thermodynamics were established. The model describes a gas as a large number of identical sub microscopic particles (atoms or molecules), all of which are in constant, rapid, random motion. Their size is assumed to be much smaller than the average distance between the particles. The particles undergo random elastic collisions between themselves and with the enclosing walls of the container. The basic version of the model describes the ideal gas, and considers no other interactions between the particles.

The kinetic theory of gases explains the macroscopic properties of gases, such as volume, pressure, and temperature, as well as transport properties such as viscosity, thermal conductivity and mass diffusivity. The model also accounts for related phenomena, such as Brownian motion.

In about 50 BCE, the Roman philosopher Lucretius proposed that apparently static macroscopic bodies were composed on a small scale of rapidly moving atoms

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all bouncing off each other. This Epicurean atomistic point of view was rarely considered in the subsequent centuries, when Aristotlean ideas were dominant.

In 1738 Daniel Bernoulli published Hydrodynamica, which laid the basis for the kinetic theory of gases. In this work, Bernoulli posited the argument, that gases consist of great numbers of molecules moving in all directions, that their impact on a surface causes the pressure of the gas, and that their average kinetic energy determines the temperature of the gas. The theory was not immediately accepted, in part because conservation of energy had not yet been established, and it was not obvious to physicists how the collisions between molecules could be perfectly elastic.

Other pioneers of the kinetic theory, whose work was also largely neglected by their contemporaries, were Mikhail Lomonosov (1747), Georges-Louis Le Sage (ca. 1780, published 1818), John Herapath (1816) and John James Waterston (1843), which connected their research with the development of mechanical explanations of gravitation. In 1856 August Krönig (probably after reading a paper of Waterston) created a simple gas-kinetic model, which only considered the translational motion of the particles.

In 1857 Rudolf Clausius developed a similar, but more sophisticated version of the theory, which included translational and, contrary to Krönig, also rotational and vibrational molecular motions. In this same work he introduced the concept of mean free path of a particle. In 1859, after reading a paper about the diffusion of molecules by Clausius, Scottish physicist James Clerk Maxwell formulated the Maxwell distribution of molecular velocities, which gave the proportion of molecules having a certain velocity in a specific range. This was the first-ever statistical law in physics. Maxwell also gave the first mechanical argument that molecular collisions entail an equalisation of temperatures and hence a tendency towards equilibrium. In his 1873 thirteen page article 'Molecules', Maxwell states: 'we are told that an 'Atom' is a material point, invested and surrounded by 'Potential Forces' and that when 'Flying Molecules' strike against a solid body in constant succession it causes what is called pressure of air and other gases.'

In 1871, Ludwig Boltzmann generalised Maxwell's achievement and formulated the Maxwell–Boltzmann distribution. Also the logarithmic connection between entropy and probability was first stated by him.

At the beginning of the 20th century, however, atoms were considered by many physicists to be purely hypothetical constructs, rather than real objects. An important turning point was Albert Einstein's (1905) and Marian Smoluchowski's (1906) papers on Brownian motion, which succeeded in making certain accurate quantitative predictions based on the kinetic theory.

The application of kinetic theory to ideal gases makes the following assumptions:

- The gas consists of very small particles. This smallness of their size is such that the sum of the volume of the individual gas molecules is negligible compared to the volume of the container of the gas. This is equivalent to

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stating that the average distance separating the gas particles is large compared to their size, and that the elapsed time of a collision between particles and the container's wall is negligible when compared to the time between successive collisions.

- The particles have the same mass.
- The number of particles is so large that a statistical treatment of the problem is well justified. This assumption is sometimes referred to as the thermodynamic limit.
- The rapidly moving particles constantly collide among themselves and with the walls of the container. All these collisions are perfectly elastic, which means the molecules are perfect hard spheres.
- Except during collisions, the interactions among molecules are negligible. They exert no other forces on one another.

Thus, the dynamics of particle motion can be treated classically, and the equations of motion are time-reversible.

More modern developments relax these assumptions and are based on the Boltzmann equation. These can accurately describe the properties of dense gases, because they include the volume of the particles. The necessary assumptions are the absence of quantum effects, molecular chaos and small gradients in bulk properties. Expansions to higher orders in the density are known as virial expansions

4.3 GAS TRANSPORT AND PUMPING

A vacuum pump is a device for creating, improving and/or maintaining a vacuum (an environment in which the pressure is below atmospheric pressure). Two basically distinct categories of vacuum pump may be considered: Gas Transfer Pumps and entrapment or capture pumps (Refer Figure 4.1).

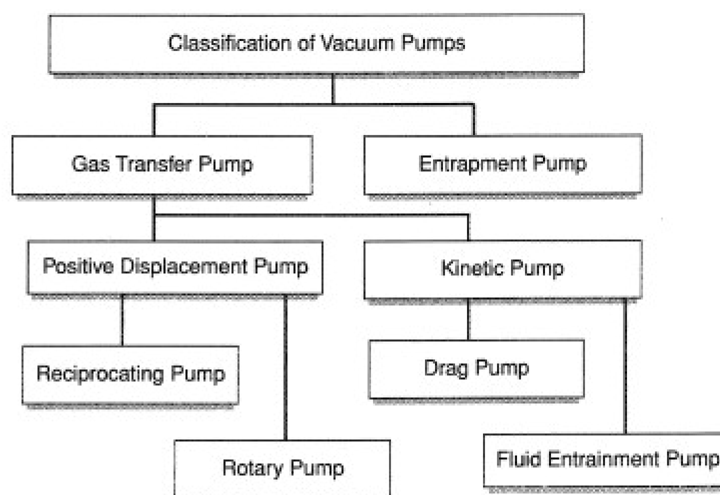


Fig. 4.1 *Classification of Vacuum Pumps*

Gas transfer pumps can be subdivided into positive displacement pumps and kinetic pumps.

Positive Displacement Vacuum Pump

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A positive displacement vacuum pump is a pump in which a volume filled with gas is cyclically isolated from the inlet, the gas being then transferred to an outlet. In most types of positive displacement pumps the gas is compressed before the discharge at the outlet. Two categories can be considered: reciprocating positive displacement pumps (e.g., piston pump) and rotary positive displacement pumps (e.g., liquid ring pump and sliding vane rotary pump).

Sliding Vane Rotary Pump

Here an eccentrically placed rotor is made to turn tangentially to the fixed surface of the stator. Normally, two vanes slide in slots in the rotor and contact the internal wall of the stator. The rotating mechanism isolates the gas from the inlet, compresses and then expels it through an outlet valve.

Kinetic Vacuum Pumps

A kinetic vacuum pump is a pump in which a momentum is imparted to the gas or the molecules in such a way that the gas is transferred continuously from the inlet to the outlet. Two categories can be considered: fluid entrainment pumps (e.g., vapour diffusion pump) and drag vacuum pumps (e.g., turbo molecular *pump*).

Diffusion Pump

Here gas transport is achieved by a series of high velocity vapour jets (normally oil vapor is used) emerging from an assembly within the pump body. In normal operation a portion of any gas arriving at the inlet jet is entrained, compressed and transferred to the next stage.

Turbo Molecular Pump

This pump contains a rotor with inclined blades moving at high speed between corresponding blades in a stator. Gas molecules entering the inlet port acquire a velocity and preferred direction superimposed on their thermal velocity by repeated collisions with the fast moving rotor. Rotational speeds for small pumps can be up to 20,000 to 90,000 revolutions per minute..

Entrapment (Capture) Vacuum Pump

A vacuum pump in which the molecules are retained by sorption; chemical combination or condensation on internal surfaces within the pump.

Sputter-Ion Pump

This makes use of the gettering principle, in which a cathode material (usually titanium) is vaporized, or sputtered, by bombardment with high velocity ions. The

active gases are pumped by chemical combination with the sputtered titanium, the inert gases by ionisation and burial in the cathode, and the light gases by diffusion into the cathode.

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Cryogenic Pump

Operation is achieved by the condensation, freezing and/or sorption of gas at surfaces maintained at extremely low temperatures, thus removing them from the gas phase in the vacuum system.

4.4 VACUUM PUMPS

1. Vacuum Pump

A vacuum pump is a device that is used to creating, improving or maintaining a vacuum in an isolated vessel (an environment in which the pressure is below the atmospheric pressure). In Figure 4.2, we can discuss the principle of vacuum pumps. Vacuum pump works same as compressors, it runs with the inlet connected to the system where vacuum is to be created and maintained the outlet open to atmosphere. Generally, compressors and vacuum pumps are similar machines. Selection of pump should be based on the range of vacuum produced, air removal rate, leak in the rate, and power needed.

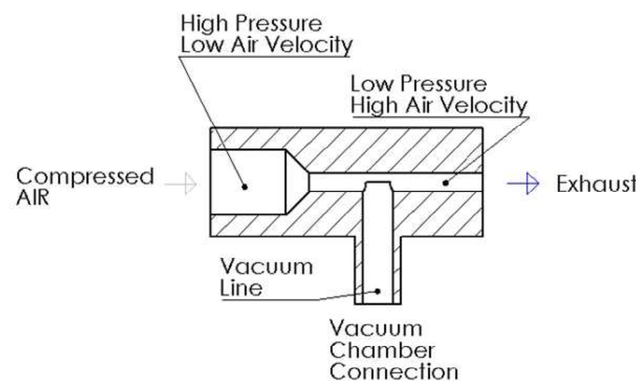


Fig. 4.2 *Schematic Diagram of Vacuum Pump*

2. Vacuum Pump Size and Pumping Speed

The following steps are adhered to while deciding a pump size for the vacuum system.

- Firstly, calculate the volume of the chamber and decide the required vacuum level.
- Calculate the total conductance of the piping in this way, we could find the effective pumping speed which is available at the evacuation port of the chamber. Calculate leakage rate and gas evolution from all surfaces of the system.

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- Decidepumpa downtime, within which we can bring down the system to a required pressure level. a

Later, we can find the effective pumping speed, required to reduce the pressure within a certain time either from using formulae or nomogram.

3. Classification of Vacuum Pumps

Vacuum pumps use various methods and two are mentioned here: gas transfer and gas capture are two of them. According to this gas, pumps are divided into two main categories as shown in Figure 4.3. Working of transfer pumps is through transferring of gas molecules through momentum exchange (kinetic action) or positive displacement, An equal number of gas molecules are discharged from the pump as entered in it and the gas is slightly above atmospheric pressure when coming out. The ratio of the exhaust pressure (coming out) to the lowest pressure obtained (coming in) is referred to as the compression ratio. Kinetic transfer pumps work on the principle of momentum transfer, directing gas towards the pump outlet to provide an increased probability of a molecule moving towards the outlet using high-speed blades or introduced vapor. Generally, Kinetic pumps do not have sealed volumes but they can achieve high compression ratios at low pressures. Working of positive displacement transfer pump is by mechanically trapping a volume of gas and moving it through the pump. Positive displacement transfer pumps are generally manufactured in multiple stages on a common drive shaft. The isolated volume is compressed to the smaller volume at a higher pressure, and finally, the compressed gas is come out to the atmosphere (or to the next pump). It is commonly used for two transfer pumps which is used in series combination to create a higher vacuum and high flow rate. For example, a turbo molecular (Kinetic) pump is generally connected in series of a scroll (Positive displacement) pump as a packaged system to increase flow rate as well as vacuum power. Capture pumps works by capturing the molecules from gas surfaces inside the vacuum chamber system. Generally, capture pumps work at low flow rates in comparison to transfer pumps but capture pumps have ability to provide ultra-high oil-free vacuum down to 10^{-12} Torr. Capture pumps are operated by utilizing cryogenic condensation process, ionic reaction or chemical reaction so it does not have any mechanically moving parts.

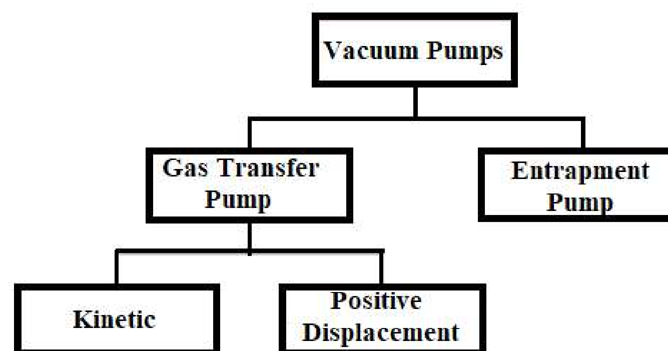


Fig. 4.3 *Types of Vacuum Pumps*

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4. Entrapment (Capture) Vacuum Pump

A vacuum pump in which molecules of the gas are retains by absorption, chemical combination, and condensation on internal surfaces within the pump. Pumps that capture gas molecules on surfaces of the vacuum system are unsurprisingly known as, Capture or Entrapment Pumps. These pumps operate at lower flow rates than vacuum pumps like transfer pumps, however, they can provide extremely high vacuum, down to 10-12 Torr. Capture pumps operate by using cryogenic condensation, ionic reaction, or chemical reaction and it does not have any moving parts, therefore it creates an oil-free vacuum.

Those Entrapment Pumps that work using chemical reactions, perform more effectively as they are usually placed inside the container where vacuum is required. Air molecules can create a thin film which is removed as the operation of the pump cause a chemical reaction to the internal surfaces of the pump. Entrapment pumps are used as positive displacement vacuum pumps and momentum transfer vacuum pumps to produce the ultra-high vacuum. The sputter-ion pump is used as of the gettering principle, in which a cathode material (by usual titanium) is vaporized, or sputtered, by bombardment with the high-velocity ions. The active gases are accelerated by chemical combination with the sputtered titanium, and the inert gases are active by ionisation and burial in the cathode, and the light gases are active by diffusion into the cathode. Cryogenic pump- Operation is achieved by the condensation, freezing, and absorption of gas at surfaces maintained at very low temperatures, thus removing them from the gas phase into the vacuum system.

5. Gas Transfer Pumps

Transfer Pumps transfer gas molecules by either momentum exchange (kinetic action) or positive displacement. The same number of gas molecules are expelled out from the pump as entered inside and the gas is slightly above atmospheric pressure when expelled. The compression ratio is defined as the ratio of the exhaust pressure or outward pressure (outlet) to the inlet pressure or lowest pressure (inlet). Gas transfer pumps can be further divided into positive displacement pumps and kinetic pumps.

6. Positive Displacement Vacuum Pump

Pumps that work mechanically trapping a volume of gas and moving it through the pump are known as positive displacement pumps. Generally, designed in multiple stages on a single drive shaft, the isolated volume is compressed to a smaller volume at high pressure, and finally, the compressed gas is expelled to either atmosphere or the next pump. To provide a higher vacuum and flow rate two transfer pumps are often used in series. As discussed earlier, positive displacement vacuum pumps are used to create low vacuums. This type of vacuum pump expands a cavity and allows the gases to flow out from the sealed environment or chamber. when the cavity is sealed and it causes depleted into the atmosphere. The principle that is used as a positive displacement vacuum pump is creating a vacuum and by expanding the volume of the container. For example,a in a manual water pump, a

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mechanism expands a small sealed cavity to create a deep vacuum. Due to pressure difference, some fluid from the chamber is pushed into the pump's small cavity and then, pump's cavity is sealed from the chamber, opened to the atmosphere, and then squeezed back to a minute size. We can consider the example of positive displacement vacuum pumps is like a diaphragm muscle expands the chest cavity, causing the volume of lungs to increase. This expansion results in creating a partial vacuum and decreasing the pressure, which is then filled by air pushed into atmospheric pressure. There are few examples of positive displacement vacuum pumps are liquid ring vacuum pumps and roots blower which are used in many industries to create a vacuum in confined space. Two categories can be assumed: reciprocating positive displacement pumps (example, Diaphragm Pumps and Piston Pumps) and Rotary positive displacement pumps (example, liquid ring pump and sliding vane rotary pump).

4.5 ROTARY, DIFFUSION AND TURBO MOLECULAR PUMPS

Rotary Pumps - Construction: The vacuum pump has a rotor and a stator.

It is a simple and most commonly used positive displacement pump as shown in Figure 4.4. It shows the internal details of a rotary pump. Construction: The vacuum pump has a rotor and a stator. Stator houses a cylindrical rotor, it has two radially machined slots opposite to each other. Two spring-loaded vanes are put in these slots which tightly rub the stator causing when it rotates. And, the rotor makes tight contact with the stator at its top. Two holes are drilled on each side of the stator from its vertical axis to which inlet and exhaust ports are connected. Internal mating surfaces are machined with high accuracy and have micron-level clearance. Stator –rotor assembly is put in oil which acts as a coolant as well as a lubricant. Mostly, the exhaust gas passes through the oil and escapes into the atmosphere. Working: Rotary pumps are typically connected to an electric motor and it drives the rotor of the pump. Centripetal causes the vanes in the spinning rotor to force them against the inner contact surface of the stator. Sometimes springs are used to improve this action. As each vane passes through the inlet port, the volume between the stator and rotor increases, and then low pressure is created inside the confined space which sucks the air from the system through the inlet port. The sucking of air continues till the vane reaches the bottom position. Another half rotation of the stator does not suck the air but compresses the entrapped air until the pressure is sufficient to open the exhaust valve. Exhaust gas escapes out through the oil to the atmosphere. As the two vanes operate simultaneously with the rotor suction, as well as compression, take place in each rotation. Rotary pumps are available in single or double-stage designs. Single-stage pumps are simple, having only one stator- rotor assembly, and they are cheap too. In a two-stage pump, the inlet port of the second stage is connected in series with the exit port of the first stage.

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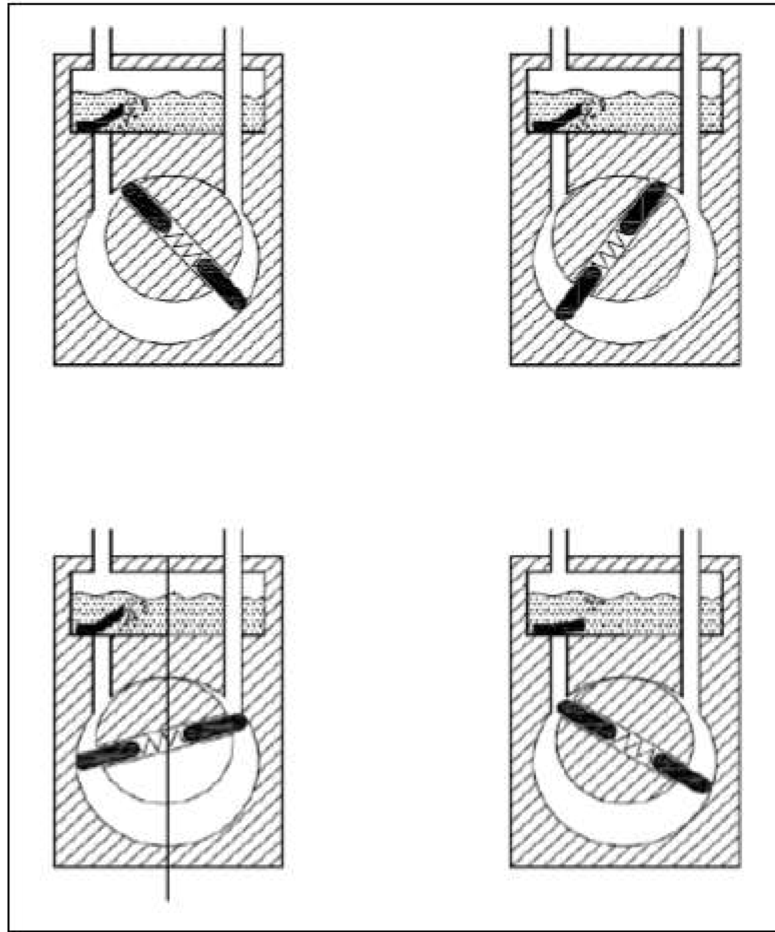


Fig. 4.4 Construction Details of Rotary Pump

Kinetic Vacuum Pumps

A kinetic vacuum pump is a pump in which momentum is transferred to the gas or the gas is transferred continuously from the inlet to the outlet. Kinetic transfer pumps are used as high-speed blades or introduced vapor to direct gas towards the outlet, working on the principle of momentum transfer. These types of the pump can be achieved by high compression ratios at low pressures but typically do not have sealed volumes. Two categories can be considered as follows:

Fluid Entrainment Pumps: Vapor Diffusion Pump

Diffusion pump– Transfer of gas is obtained by a series of high-velocity vapor jets (normally oil vapor is used) coming out from an assembly within the pump body. During normal operation, a portion of any gas that is reached at the inlet jet is entrained, compressed, and later transferred to the next stage.

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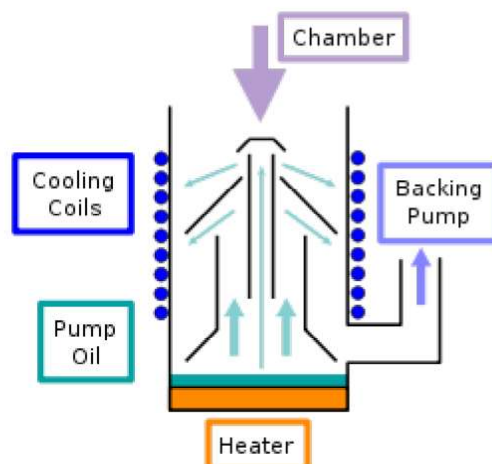


Fig. 4.5 *Schematic Diagram of Diffusion Pump*

The oil diffusion pump is worked as oil of low vapor pressure. A high-speed jet of the Oil is worked by boiling the Oil and directing the vapor through a jet assembly. Note that the oil is gaseous when entering the nozzles. Within the spouts, the flow changes from laminar, to supersonic and then molecular. Often several jets are used in series to increase the pumping action. The outer side of the diffusion pump is cooled through airflow or a water line. As the vapor jet enters the outer cooled side of the diffusion pump, the working of fluid condenses and fluid is recovered and comes back to the boiler. The pumped gases continue flowing to the base of the pump at increased pressure, flowing out through the diffusion pump outlet, where they are compressed to medium pressure by the secondary mechanical fore pump and depleted. Directly, diffusion pumps cannot be discharged into the atmosphere, so a mechanical fore pump is typically used to discharge the diffusion pump and to maintain an outlet pressure around 0.1 bar. Diffusion pumps have no moving parts and as a result, are quite long-lasting and reliable. Diffusion pumps can work overpressure ranges of 10^{-10} to 10^{-2} bar. They are operated only by convection and thus have very low energy efficiency and low cost per unit pumping speed when compared with other types of pumps used in the same vacuum range. One major disadvantage of diffusion pumps is the inclination to backstream oil into the chamber being evacuated. This oil can pollute surfaces inside the chamber or upon contact with hot filaments or electrical discharges may result in carbon-based or siliceous deposits. mostly, cold traps and baffles are utilized between the chamber and the diffusion pump to reduced back streaming, although this results in some loss of pumping ability. The oil of a diffusion pump cannot be an exhibit to the atmosphere when hot. If oil exhibit to the atmosphere, the oil will burn and has to be replaced.

Drag Vacuum Pumps: Turbo Molecular Pump

Turbo Molecular Pump: This pump contains a rotor with inclined blades moving at a very high speed between corresponding blades in a stator. Gas molecules

entering the inlet port achieve a velocity and favorable direction superimposed on their thermal velocity by repeated collisions with the fast-moving rotor. Small pumps are having rotational speed up to 90,000 rev min^{-1}.

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Principle: It works on the principle of momentum transfer. With a rapidly rotating rotor, the gas molecules' initially nondirected thermal motion is converted to a directed motion. Hence, the pumping is obtained by directing the gas molecules from the inlet flange to the burst port where a backing pump has already been connected. Generally, this pump is used to clear the chamber which is already in a vacuum range, below 10^{-3} bar which comes under the molecular flow range**.** In molecular flow range, since the mean free path of the gas molecules is more than the spacing between rotor and stator blades, molecules that are being collided with the blades get adsorbed with rotor blades and after some time on continuing the rotation of the rotor, the thermal molecular speeds increased by absorbing momentum from rotor blades. Due to this increased momentum, molecules get detached from the preceding rotor blades and get attached to the next stator blade. This process will continue until the molecules reach the exhaust port. In the molecular flow range when the pressure is below 10^{-3} bar the mean free path is larger than the clearance between stators. Therefore the molecules first come in contact with rotor blades as compared to molecules each other. This is the reason why this pump works efficiently within the molecular flow region. Whereas when pressure exceeds the cross-over limit, i.e., in laminar flow range at pressure over 10^{-1} bar intermolecular collisions will be measured. Due to this reason, the turbo-molecular pump is able of measuring a system that is kept at atmospheric pressure. Afore vacuum pump is always fitted with a turbo molecular pump to bring down the pressure from atmospheric to crossover pressure. Once the system pressure is reached crossover pressure, then we can operate the turbo pump for further pump down process. Its speed varies from 30,000-90,000 rpm.

The crossover pressure of turbo-molecular pumps is around 1 Torr. This is a factor often-times higher pressure than the maximum designed crossover pressure for most oil vapor diffusion pumps (100 mTorr). At pressures above 1 Torr, the turbo pump blades will be slowed down by collisions with the gas molecules such that the motor will be overload and the rotational velocity of the rotor will decrease to a speed that is unproductive for pumping gas. Unlike diffusion pumps, turbo pumps do have moving parts that can cause vibration which may badly affect some accuracy instruments including scanning electron microscopes and surface science probes. A 60 or 120 Hz vibration typically is caused by a mechanical backing pump, while a high-frequency vibration is due to imbalances in the turbo pump rotor. Most vacuum applications are not accurate to this minute amount of vibration, but if vibration must be held to a minimum, and the pumping characteristics of a turbo pump are required, a magnetically

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levitated rotor design may give the solution. In such type of turbopump normal (but oil-free) bearings are only used on start-up and shut-down of the turbo. During normal operation the rotor is suspended above the bearings by well-matched sets of strong magnets, virtually neglecting all mechanical vibration. Magnetically levitated turbo pumps are designed to operate for very long periods with very few breaking. Each time a magnetically levitated turbo pump is started or stopped, the oil-free mechanical bearings suffer wear and finally will require replacement. Beyond reduction of vibration, the magnetically floated rotor design turbo offers the option of mounting in any orientation, as there is no oil sump as in most conventional turbo pumps.

4.6 PIRANI AND PENNING GAUGES

Pirani Vacuum Gauge

The Pirani gauge consists of a metal filament (usually platinum) hanged in a tube that is connected to the system whose vacuum is to be measured. The connection is usually made either by a ground glass joint or a flanged o-ring. The filament is connected to an electrical circuit from which, after measurement, a pressure reading may be taken. The metal connector is sealed with a conducting wire (platinum filament) gets heated when an electric current flows through it. This wire suspended in gas will lose heat to the gas as its molecules collide with the wire and extract heat. As the gas pressure is decreased (by the vacuum pumps) the number of molecules present will fall, the conductivity of the surrounding media will fall and the wire will lose heat more slowly. Measuring the heat loss is an indirect indication of pressure. The electrical resistance of the wire changes with its temperature, so the measurement of resistance also specifies the temperature of the wire. Now the change in resistance of the filament is calculated using the bridge. This change in resistance of the Pirani gauge filament becomes a measure of the applied pressure when weighed. In most of the systems, the wire is maintained at a constant resistance R by controlling the current I through the wire. The resistance can be set using a bridge circuit. The power delivered to the wire is I^2R, and the same power is transferred to the gas. The current required to attain this balance is therefore a measure of the vacuum. The gauge may be used for measuring pressures between 0.5 Torr Penning gauge to 10^{-3} Torr. The thermal conductivity and heat capacity of the gas may affect the reading from the meter, and therefore the apparatus may need evaluation before accurate readings are obtainable. For measuring lower pressure measurement other instruments are used.

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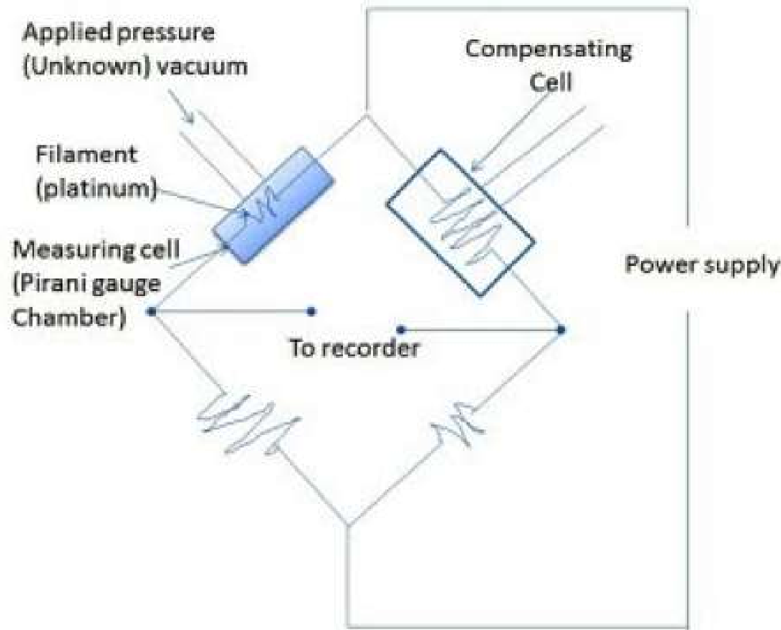


Fig. 4.6 *Schematic Diagram of Pirani Gauge*

Penning Vacuum Gauge

The Penning vacuum gauge is a cold cathode type ionisation gauge consisting of two electrodes anode and cathode. The outer cylinder of the gauge is of cathode and it is at room temperature. The anode consists of a tungsten wire rotated in the center of the tube A potential difference of about 2 to 3 kV is applied between anode and cathode through current limiting resistors. A magnetic field is applied at right angles to the plane of the electrodes by a permanent magnet having approximately 800 gausses magnetic field which will increase the ionization current. The electrons emitted from the cathode (gauge head body) of the gauge head are deflected by using a magnetic field applied at right angles to the plane of the electrodes and are made to take a helical path before reaching the anode loop. Thus, following the very long path the electrons ionize the gas through collision, even at low pressures. The secondary electrons produced through ionization and themselves perform similar oscillations and the rate of ionization increases rapidly. At last, the electrons are captured by the anode, and equilibrium is reached when the number of electrons produced per second by ionization is the sum of positive ion current to the cathode and the electron (negative ion) current to the anode. This small current is calculated to give a measure of the pressure of the gas and hence the chamber to which it is attached. The Cold Cathode Penning gauge can measure vacuum from 10^{-2} to 10^{-7} Torr or bar.

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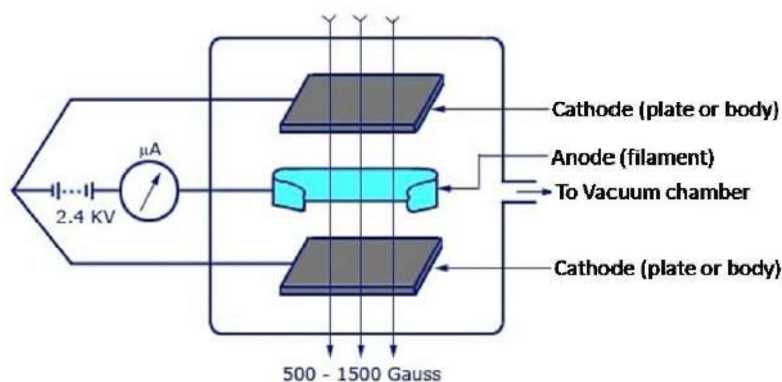


Fig. 4.7 *Schematic Diagram Penning Vacuum Gauge*

Check Your Progress

1. Explain about the kinetic theory of gas.
2. What is the vacuum pump?
3. What do you understand by diffusion pump?
4. Define the vacuum pump.
5. How does the gas transfer pumps work?
6. Explain the kinetic vacuum pumps.
7. Define the term turbo molecular pump.
8. What is Pirani vacuum gauge?
9. Explain the Penning vacuum gauge.

4.7 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The kinetic theory of gases explains the macroscopic properties of gases, such as volume, pressure, and temperature, as well as transport properties such as viscosity, thermal conductivity and mass diffusivity. The model also accounts for related phenomena, such as Brownian motion.
2. A vacuum pump is a device for creating, improving and/or maintaining a vacuum (an environment in which the pressure is below atmospheric pressure). Two basically distinct categories of vacuum pump may be considered: Gas Transfer Pumps and entrapment or capture pumps.
3. Gas transport is achieved by a series of high velocity vapour jets (normally oil vapour is used) emerging from an assembly within the pump body. In normal operation a portion of any gas arriving at the inlet jet is entrained, compressed and transferred to the next stage.

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4. A vacuum pump is a device that is used to creating, improving or maintaining a vacuum in an isolated vessel (an environment in which the pressure is below the atmospheric pressure).
5. Transfer Pumps transfer gas molecules by either momentum exchange (kinetic action) or positive displacement. The same number of gas molecules are expelled out from the pump as entered inside and the gas is slightly above atmospheric pressure when expelled. The compression ratio is defined as the ratio of the exhaust pressure or outward pressure (outlet) to the inlet pressure or lowest pressure (inlet).
6. A kinetic vacuum pump is a pump in which momentum is transferred to the gas or the gas is transferred continuously from the inlet to the outlet. Kinetic transfer pumps are used as high-speed blades or introduced vapour to direct gas towards the outlet, working on the principle of momentum transfer.
7. This pump contains a rotor with inclined blades moving at a very high speed between corresponding blades in a stator. Gas molecules entering the inlet port achieve a velocity and favourable direction superimposed on their thermal velocity by repeated collisions with the fast-moving rotor. Small pumps are having rotational speed up to 90,000 rev min^{-1}.
8. The Pirani gauge consists of a metal filament (usually platinum) hanged in a tube that is connected to the system whose vacuum is to be measured. The connection is usually made either by a ground glass joint or a flanged o-ring. The filament is connected to an electrical circuit from which, after measurement, a pressure reading may be taken. The metal connector is sealed with a conducting wire (platinum filament) gets heated when an electric current flows through it.
9. The Penning vacuum gauge is a cold cathode type ionization gauge consisting of two electrodes anode and cathode. The outer cylinder of the gauge is of cathode and it is at room temperature. The anode consists of a tungsten wire rotated in the centre of the tube a potential difference of about 2 to 3 kV is applied between anode and cathode through current limiting resistors.

4.8 SUMMARY

- The kinetic theory of gases explains the macroscopic properties of gases, such as volume, pressure, and temperature, as well as transport properties , such as viscosity, thermal conductivity and mass diffusivity. The model also accounts for related phenomena, such as Brownian motion.
- The particles undergo random elastic collisions between themselves and with the enclosing walls of the container. The basic version of the model

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describes the ideal gas, and considers no other interactions between the particles.

- The kinetic theory of gases explains the macroscopic properties of gases, such as volume, pressure, and temperature, as well as transport properties, such as viscosity, thermal conductivity and mass diffusivity. The model also accounts for related phenomena, such as Brownian motion.
- In 1738 Daniel Bernoulli published Hydrodynamica, which laid the basis for the kinetic theory of gases. In this work, Bernoulli posited the argument, that gases consist of great numbers of molecules moving in all directions, that their impact on a surface causes the pressure of the gas, and that their average kinetic energy determines the temperature of the gas.
- A vacuum pump is a device that is used to creating, improving or maintaining a vacuum in an isolated vessel (an environment in which the pressure is below the atmospheric pressure).
- A positive displacement vacuum pump is a pump in which a volume filled with gas is cyclically isolated from the inlet, the gas being then transferred to an outlet. In most types of positive displacement pumps the gas is compressed before the discharge at the outlet.
- Gas transport is achieved by a series of high velocity vapour jets (normally oil vapour is used) emerging from an assembly within the pump body. In normal operation a portion of any gas arriving at the inlet jet is entrained, compressed and transferred to the next stage.
- A vacuum pump in which the molecules are retained by sorption; chemical combination or condensation on internal surfaces within the pump.
- Operation is achieved by the condensation, freezing and/or sorption of gas at surfaces maintained at extremely low temperatures, thus removing them from the gas phase in the vacuum system.
- A vacuum pump is a device that is used to creating, improving or maintaining a vacuum in an isolated vessel (an environment in which the pressure is below the atmospheric pressure).
- Positive displacement transfer pumps are generally manufactured in multiple stages on a common drive shaft. The isolated volume is compressed to the smaller volume at a higher pressure, and finally, the compressed gas is come out to the atmosphere (or to the next pump).
- Transfer Pumps transfer gas molecules by either momentum exchange (kinetic action) or positive displacement. The same number of gas molecules are expelled out from the pump as entered inside and the gas is slightly above atmospheric pressure when expelled.

- Pumps that work mechanically trapping a volume of gas and moving it through the pump are known as positive displacement pumps. Generally, designed in multiple stages on a single drive shaft, the isolated volume is compressed to a smaller volume at high pressure, and finally, the compressed gas is expelled to either atmosphere or the next pump.
- The vacuum pump has a rotor and a stator. Stator houses a cylindrical rotor, it has two radially machined slots opposite to each other. Two spring-loaded vanes are put in these slots which tightly rub the stator causing when it rotates.
- A kinetic vacuum pump is a pump in which momentum is transferred to the gas or the gas is transferred continuously from the inlet to the outlet. Kinetic transfer pumps are used as high-speed blades or introduced vapour to direct gas towards the outlet, working on the principle of momentum transfer.
- Transfer of gas is obtained by a series of high-velocity vapour jets (normally oil vapour is used) coming out from an assembly within the pump body. During normal operation, a portion of any gas that is reached at the inlet jet is entrained, compressed, and later transferred to the next stage.
- The Pirani gauge consists of a metal filament (usually platinum) hanged in a tube that is connected to the system whose vacuum is to be measured. The connection is usually made either by a ground glass joint or a flanged o-ring.
- The Penning vacuum gauge is a cold cathode type ionization gauge consisting of two electrodes anode and cathode. The outer cylinder of the gauge is of cathode and it is at room temperature.

4.9 KEY WORDS

- **Kinetic theory of gases:** The kinetic theory of gases explains the macroscopic properties of gases, such as volume, pressure, and temperature, as well as transport properties such as viscosity, thermal conductivity and mass diffusivity. The model also accounts for related phenomena, such as Brownian motion.
- **Vacuum pump:** A vacuum pump is a device for creating, improving and/or maintaining a vacuum (an environment in which the pressure is below atmospheric pressure). Two basically distinct categories of vacuum pump may be considered: Gas Transfer Pumps and entrapment or capture pumps.
- **Kinetic vacuum pump:** A kinetic vacuum pump is a pump in which a momentum is imparted to the gas or the molecules in such a way that the gas is transferred continuously from the inlet to the outlet.

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- **Gas transfer pumps:** Transfer Pumps transfer gas molecules by either momentum exchange (kinetic action) or positive displacement. The same number of gas molecules are expelled out from the pump as entered inside and the gas is slightly above atmospheric pressure when expelled.
- **Diffusion pump:** Transfer of gas is obtained by a series of high-velocity vapour jets (normally oil vapour is used) coming out from an assembly within the pump body. During normal operation, a portion of any gas that is reached at the inlet jet is entrained, compressed, and later transferred to the next stage.

4.10 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Explain the concept of kinetic theory of gases.
2. Define the kinetic vacuum pumps.
3. What do you mean by gas transport?
4. Write the process of pumping.
5. Explain the importance of rotary and diffusion pumps.
6. Define the turbo molecular pump.
7. Why are the Pirani and Penning gauges used?

Long-Answer Questions

1. Discuss briefly the concept of kinetic theory of gases with the help of examples.
2. Analyses the gas transport and pumping.
3. Describe the vacuum gauges.
4. Explain about the rotary, diffusion and turbo molecular pumps.
5. Briefly discuss about the Pirani and Penning gauges with the help of examples.

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UNIT 5 THIN FILMS BY EVAPORATION

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Structure

5.0 INTRODUCTION

Thin Film Deposition is a well-known technique to deposit a thin film of sample material that ranges from a few nanometers to about 100 micrometers, or in other words the thickness of atomic dimension onto a 'Substrate', or on a previously deposited film layer. Thin Film Deposition techniques are an essential need have today's semiconductor and electronics industry like solar panels, CDs, disk drives, and optical devices industries. Thin Film Deposition can be divided into two broad categories - Chemical deposition method and Physical vapor deposition Coating method. Physical Vapor Deposition is used in a wide range of technologies applications where the sample material is vapourised from a source boat and deposited on a substrate using any of one from mechanical, electromechanical, or thermodynamic processes. Nowadays two most commonly used deposition techniques for Physical Vapor Deposition or PVD are the Thermal Evaporation Technique and Sputtering Technique. Physical evaporation is one of the basic and oldest methods used for depositing metal films. Metals like Aluminum, gold, and other metals are heated using current elements in a boat to the point of vaporisation and then freed to evaporate to form a thin film covering the surface of the substrate. All film deposition needs an under a vacuum or very carefully controlled atmosphere. Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface. After leaving the source material surface these free atoms travel through the vacuum chamber and got coated on a substrate positioned above the evaporating material.

In this unit, you will study about thin films by thermal evaporation, thickness measurement - quartz crystal method.

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5.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss about the thin films by thermal evaporation
- Explain the thickness measurement by quartz crystal method

5.2 THIN FILMS BY THERMAL EVAPORATION

1. Thermal Vacuum Evaporation

The thermal Evaporation Technique involves heating and vapourising a solid material that will be used to coat a substrate inside a high evacuated vacuum chamber until it starts to evaporate producing a vapor phase. Inside the evacuated vacuum deposition chamber, even a low vapor pressure is sufficient to raise a vapor cloud which is enough to deposit thin film. This evaporated material in a vacuum chamber now creates a vapor stream that travels through the vacuum without reacting or scattering against other atoms or walls of the chamber. It traverses the chamber and hits the substrate, sticking to it as a coating or thin-film substrate. Two primary methods used for heating the source material during the process of Thermal Evaporation. One includes Filament Evaporation, as it is achieved with a simple electrical heating element or filament inside a boat. The other heat method used electron beam or E-Beam Evaporation where an electron beam is focused at the source material to evaporate it and convert it into the gas phase. The main advantages of thin Film Evaporation systems including high deposition rates, real-time deposition and thickness control, and (with suitable physical configuration) good evaporant stream directional control for processes such as Lift Off to achieve directly patterned coatings.

Basic Principle: Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface. After leaving the source material surface these free atoms travel through the vacuum chamber and got coated on a substrate positioned above the evaporating material.

Procedure: In thermal evaporation techniques, depending on the availability of tools and types of source and substrate materials used for deposition different methods can be applied to heat the source material. The instrument available in the laboratory utilised either resistance heating or electron beam heating, usually several KeV, from an electron beam gun (electron beam heating).

5.3 THICKNESS MEASUREMENT- QUARTZ CRYSTAL METHODS

It has been well known that the film deposition and their structure of vacuum are highly dependent on the deposition parameters like a vacuum, distance between

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source and substrate. Since the thin film formation and the resulting structure of the films decide to a large extent the physical properties. since these properties highly dependent on the same deposition parameters hence it becomes important that as many of these parameters must be under close control as possible during the deposition of thin-film if vacuum deposited thin films are to be made reproducible in every respect.

The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardised to measure thickness after removed from the deposition chamber. Only a few measurement methods are suitable for real-time monitoring of film thickness during thin film growth on the substrate. The very useful and accurate gravimetric technique to determine both thin film deposition rate and thickness of thin-film utilised a quartz crystal oscillator. It is based on the fact of using the thickness-shear mode of piezoelectric quartz crystal. A change in the resonant frequency of the crystal oscillator during the process of thin-film deposition varies linearly with the deposited mass on the electrode of the crystal. If the crystal sensor is made to place near the substrate during the process of deposition the as the coating on the crystal increases its mass will lower its resonant frequency. Here we discuss the application of quartz-crystal monitors in a thin film deposition chamber of ultrahigh vacuum pressure setup. Inside this kind of chamber, there are two holders for quartz oscillators. The mass deposited from the source material and its evaporation rate is controlled during deposition by a monitoring quartz sensor mounted and from the side of the substrate holder and so the crystal does not receive the same deposition rate as the substrate.

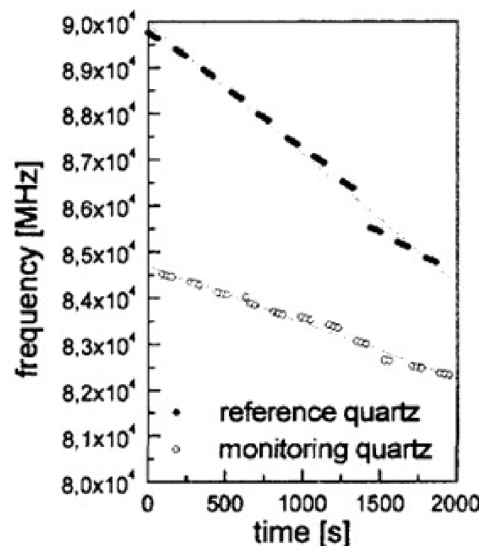


Fig. 5.1 *the Frequency changes of Reference and Monitoring Quartz Crystals as a Function of Evaporation Time. Solid Lines Represent Linear Fit Results*

There is no direct correlation between the mass of the crystal and the resonant frequency, therefore a tooling factor correction has to be determined. For this purpose, a reference quartz oscillator is mounted on the backside of a rotatable thin film substrate holder. The determination of tooling factor is performed by source material evaporation in one process on both, monitoring and reference, quartz crystals. The calibration of quartz crystal monitors is done by silver evaporation with the evaporator. The frequency was sampled every 30 s during 30 min of evaporation. Registered changes of frequency are shown in Figure 5.1. The tooling factor between reference and monitoring quartz determined as a ratio of slopes of fitted lines were equal to 2.2(2). In the next step, silver was evaporated on a glass substrate with a deposition rate of about 9 A/min. The observed frequency change corresponds to the deposition of 20.8 mg of silver. Assuming the uniform film thickness and its density as for bulk system it is equivalent to a thickness of 198 A. This result is in very good agreement with a thickness measured by X-ray reflectometry.

Check Your Progress

1. Explain the thermal evaporation technique.
2. What are the two primary methods for heating the source material?
3. What is the significant parameter of thickness measurement?

5.4 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The thermal Evaporation Technique involves heating and vapourising a solid material that will be used to coat a substrate inside a high evacuated vacuum chamber until it starts to evaporate producing a vapor phase. Inside the evacuated vacuum deposition chamber, even a low vapor pressure is sufficient to raise a vapor cloud which is enough to deposit thin film.
2. Two primary methods used for heating the source material during the process of Thermal Evaporation. One includes Filament Evaporation, as it is achieved with a simple electrical heating element or filament inside a boat.
3. The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardized to measure thickness after removed from the deposition chamber.

5.5 SUMMARY

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- The thermal Evaporation Technique involves heating and vapourising a solid material that will be used to coat a substrate inside a high evacuated vacuum chamber until it starts to evaporate producing a vapor phase. Inside the evacuated vacuum deposition chamber, even a low vapor pressure is sufficient to raise a vapor cloud which is enough to deposit thin film.
- Two primary methods used for heating the source material during the process of Thermal Evaporation. One includes Filament Evaporation, as it is achieved with a simple electrical heating element or filament inside a boat. The other heat method used electron beam or E-Beam Evaporation where an electron beam is focused at the source material to evaporate it and convert it into the gas phase.
- The main advantages of thin Film Evaporation systems including high deposition rates, real-time deposition and thickness control, and (with suitable physical configuration) good evaporant stream directional control for processes such as Lift Off to achieve directly patterned coatings.
- In thermal evaporation techniques, depending on the availability of tools and types of source and substrate materials used for deposition different methods can be applied to heat the source material. The instrument available in the laboratory utilised either resistance heating or electron beam heating, usually several KeV, from an electron beam gun (electron beam heating).
- The thin film formation and the resulting structure of the films decide to a large extent the physical properties. since these properties highly dependent on the same deposition parameters hence it becomes important that as many of these parameters must be under close control as possible during the deposition of thin-film if vacuum deposited thin films are to be made reproducible in every respect.
- The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardized to measure thickness after removed from the deposition chamber.
- A change in the resonant frequency of the crystal oscillator during the process of thin-film deposition varies linearly with the deposited mass on the electrode of the crystal. If the crystal sensor is made to place near the substrate during the process of deposition the as the coating on the crystal increases its mass will lower its resonant frequency.
- The application of quartz-crystal monitors in a thin film deposition chamber of ultrahigh vacuum pressure setup.

- The mass deposited from the source material and its evaporation rate is controlled during deposition by a monitoring quartz sensor mounted and from the side of the substrate holder and so the crystal does not receive the same deposition rate as the substrate.
- There is no direct correlation between the mass of the crystal and the resonant frequency, therefore a tooling factor correction has to be determined. For this purpose, a reference quartz oscillator is mounted on the backside of a rotatable thin film substrate holder.
- The determination of tooling factor is performed by source material evaporation in one process on both, monitoring and reference, quartz crystals. The calibration of quartz crystal monitors is done by silver evaporation with the evaporator.

NOTES

5.6 KEY WORDS

- **Thermal evaporation:** Technique involves heating and vapourising a solid material that will be used to coat a substrate inside a high evacuated vacuum chamber until it starts to evaporate producing a vapor phase. Inside the evacuated vacuum deposition chamber, even a low vapor pressure is sufficient to raise a vapor cloud which is enough to deposit thin film.
- **Basic principle:** Thermal Evaporation technique work on the principle that the material is heated in a vacuum chamber until it provides enough energy to surface atoms leave the surface. After leaving the source material surface these free atoms travel through the vacuum chamber and got coated on a substrate positioned above the evaporating material.
- **Thickness measurement:** The thickness is the most significant parameter among all because it influences almost all film properties of the thin film. The different types of films and their applications have generated different techniques to measure the thickness of the film. Most methods used for thickness measurements have been standardized to measure thickness after removed from the deposition chamber.

5.7 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Give the definition thin films by thermal evaporation.
2. What is the principle of thermal evaporation technique?
3. Write the procedure of thermal evaporation technique.

4. Give the uses of thickness measurement.
5. Explain the quartz crystal method.

Long-Answer Questions

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1. Briefly explain the thermal evaporation technique.
2. Discuss in detail about the thickness measurement by quartz crystal method.

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UNIT 6 THIN FILMING BY EPITAXY

NOTES

Structure

6.0 INTRODUCTION

Epitaxy refers to a type of crystal growth or material deposition in which new crystalline layers are formed with one or more well-defined orientations with respect to the crystalline substrate. The deposited crystalline film is called an epitaxial film or epitaxial layer. The relative orientation(s) of the epitaxial layer to the crystalline substrate is defined in terms of the orientation of the crystal lattice of each material. For epitaxial growth, the new layer must be crystalline and each crystallographic domain of the over layer must have a well-defined orientation relative to the substrate crystal structure. Amorphous growth or multi crystalline growth with random crystal orientation does not meet this criterion. For most technological applications, single domain epitaxy, which is the growth of an over layer crystal with one well-defined orientation with respect to the substrate crystal, is preferred.

The term epitaxy comes from the Greek roots epi, meaning ‘Above’, and taxis, meaning ‘An Ordered Manner’.

One of the main commercial applications of epitaxial growth is in the semiconductor industry, where semiconductor films are grown epitaxially on semiconductor substrate wafers.For the case of epitaxial growth of a planar film atop a substrate wafer, the epitaxial film's lattice will have a specific orientation relative to the substrate wafer’s crystalline lattice such as the [001] Miller index of the film aligning with the [001] index of the substrate. In the simplest case, the epitaxial layer can be a continuation of the same exact semiconductor compound as the substrate; this is referred to as homoepitaxy. Otherwise, the epitaxial layer will be composed of a different compound; this is referred to as heteroepitaxy.

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Epitaxy is used in nanotechnology and in semiconductor fabrication. Indeed, epitaxy is the only affordable method of high quality crystal growth for many semiconductor materials. In surface science, epitaxy is used to create and study monolayer and multilayer films of adsorbed organic molecules on single crystalline surfaces. Adsorbed molecules form ordered structures on atomically flat terraces of single crystalline surfaces and can directly be observed via scanning tunnelling microscopy. In contrast, surface defects and their geometry have significant influence on the adsorption of organic molecules.

The Lattice Constant of a semiconductor is described by the atomic spacing (in Angstrom) in the semiconductor crystal of that material. Growing films of different types of semiconductor material on top of each other are observed to create a boundary region where the two crystal structures meet.

In this unit, you will study about the epitaxy, structural aspects, lattice misfit and imperfections, liquid phase epitaxy, vapour phase epitaxy, epitaxy of compound semiconductor, applications.

6.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss about epitaxy
- Explain the structural aspects
- Describe state of lattice misfit imperfection
- Define the liquid phase epitaxy
- Understand the epitaxy of compound semiconductor
- Provide the important applications

6.2 EPITAXY

Epitaxy (epi means 'upon' and taxis means 'ordered') is a term applied to processes that are used to grow a thin crystalline layer (film) on a crystalline substrate. The seed crystal in epitaxial processes is used as the substrate. Unlike the Czochralski process, crystalline thin films can be easily grown below the melting point using film deposition methods, such as Chemical Vapour Deposition (CVD), Molecular Beam Epitaxy (MBE), etc. When a material is made to grown epitaxially on a crystalline substrate of the same material, the process is called homoepitaxy, an example of which is depicted in Figure 6.1. Contrary to this, if the layer and substrate are made of different kinds of materials, such as AlxGa1-xAs on GaAs, then this process is termed heteroepitaxy. Basically, in process of heteroepitaxy, the crystal structures of the layer and the substrate must be similar to attain good crystalline integrity. The performance of many devices, such as CMOS

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(Complementary MOS) and DRAM (Dynamic Random Access Memory), can be enhanced by employing epitaxial wafers. Epitaxial wafers have two fundamental advantages over bulk wafers. First, device engineers can control the doping profiles not attainable through other conventional means, such as diffusion or ion implantation. Secondly, we can make different the physical and chemical properties of the epitaxial layers from the bulk materials.

6.3 STRUCTURAL ASPECTS

Two different kinds of epitaxy are recognized:

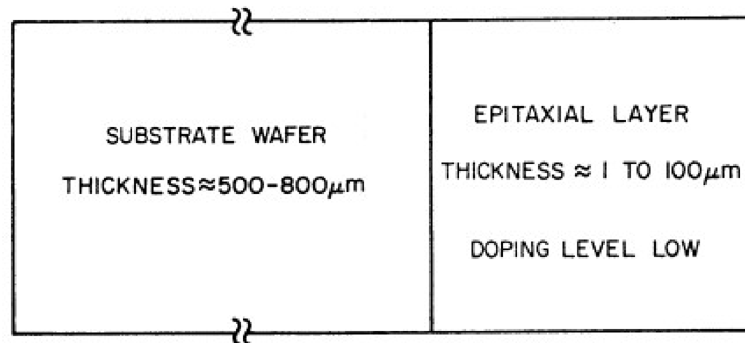


Fig. 6.1 *Cross-Sectional Schematic of a Typical Epitaxial Layer and Substrate*

Homo-Epitaxy Growth

In this kind of growth the epitaxial layer and substrate are of the same material. For example- the Chemical vapour deposition of a single-crystal silicon thin film on a single-crystal silicon substrate having the same crystallographic orientation hence the process is known as homoepitaxy, which is accomplished by hydrogen reduction of dichlorosilane vapour.

Hetero-Epitaxy Growth

In this kind of growth the epitaxial layer and the substrate both are of a different material. For example, if a single-crystal film of silicon is deposited on any crystal substrate except silicon hence this process is termed heteroepitaxy. Layers of single-crystal compound semiconductors are created to a thickness of a few atomic size dimension layers by molecular beam epitaxy.

6.4 LATTICE MISFIT AND IMPERFECTIONS

This specially defines the situation when two materials having different lattice constants are brought together by deposition of the layer of one material on top of the second. The lattice mismatch prevents the growth of defect-free epitaxial film unless the thickness in the thin film is below a certain critical thickness. The Lattice

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Constant of a semiconductor is described by the atomic spacing (in Angstroms) in the semiconductor crystal of that material. Growing films of different types of semiconductor material on top of each other are observed to create a boundary region where the two crystal structures meet. If the lattice constants are significantly different from each other, the mismatching atomic positions in the crystal at the boundaries can cause strain, resulting in cracks or dislocations that generally propagate through the structure. This can be a terrible thing for the active region, as it interrupts the specifically designed superlattice that is used to define the quantum structure. Because growing material on top of another with a significantly different lattice constant, a buffer layer can be utilised. This layer eases the lattice constant of the structure from one value to another in gradual steps. It can also catch roving striations, shielding the laser core. The misfit dislocation originates from threading dislocations at the film-substrate interface.

- The dislocation pierces through the substrate and the film.
- As it grows, it glides and bends in a slip plane.
- Above the critical thickness (dc) the increasing strain allows a break and the film dislocation separates from the originating defect, leaving behind a stable misfit dislocation.
- If the lattice mismatch is less than ~9%, the initial layers of the film will grow pseudomorphically.
- Therefore very thin films strain elastically to have the same inter-atomic spacing as the substrate.
- As film thickness increases, the rising strain will eventually cause a series of misfit dislocations separated by regions of a relatively good fit. As such they are equilibrium theories a.
- There is a critical film thickness, dc, beyond which dislocations are introduced.

6.5 LIQUID PHASE EPITAXY

Historically, in the early age of technology, compound semiconductor growth was performed by using liquid phase epitaxial techniques and to date, numerous optoelectronic devices are still fabricated by using the same process. The threshold current values of the best Double Heterostructure (DH) Molecular Beam Epitaxy (MBE) Lasers are typically compared to LPE results. There are many variants of the LPE process, but in this approach most common to multilayer film growth a graphite holder used to slides a sample between materials melts of different compositions. A schematic of a graphite diagram of the slider LPE system is shown in Fig. 6.2(a). The working temperature and composition of materials melt determine the stoichiometry and deposition rate. Film growth obtained from the controlled cooling of the supersaturated melt. Different bins are required for each layer of

different alloy compositions. Thorough knowledge of the alloy phase diagram is necessary to control the film composition with accuracy. Weighted amounts of impurities are mixed into the materials melts to control doping concentration. Dopants having relatively high distribution coefficients are not easily controlled. LPE has many advantages like low capital cost, high deposition rates, high material purity, no toxic gases, and a relatively wide selection of dopants. But some disadvantages also the inability to produce abrupt (monolayer) interfaces and poor large area uniformity; and difficulty in changing stoichiometry ratio and controlling the reproducibility of ternary III-V compounds. Advances in LPE equipment have allowed superlattice structures of 200-300 Å thick layers to be produced. Despite such progress, LPE is not considered amenable to high-volume automated manufacturing.

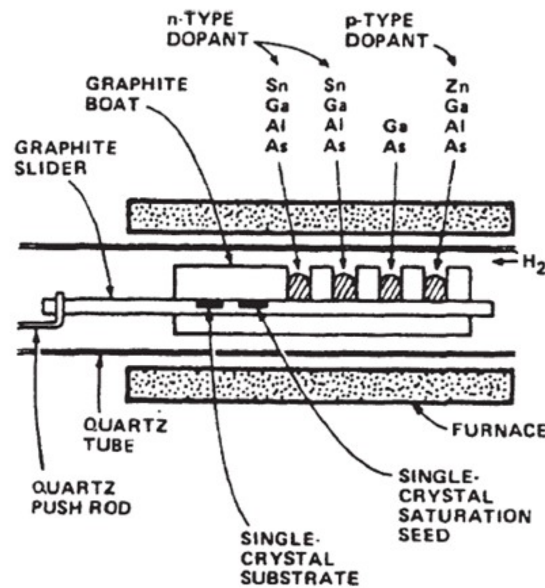


Fig. 6.2(a) *Alternative Epitaxial Processes: Liquid Phase Epitaxy*

Liquid-Phase Epitaxy Application

LPE is mainly applied for the thermally-controlled overgrowth of single-crystalline thin films using compound semiconductors and magnetic garnets from the melt on the top of the single-crystal substrate. This is a relatively older and easy technique that has been successfully applied in the electronics industry for fabricating optoelectronic and other VLSI device components. However, in comparison to the MBE, LPE is limited because of poor uniformity on a large area and surface morphology. Various additional film formation techniques that are used industrially have not been discussed here, because they are fundamentally thick-film techniques. These methods include powder or glass frit sedimentation and centrifugation, dipping, screen-printing, tape transfer, fluidized bed coating, and electrostatic spraying, all of above followed by thermal treatments for drying and fusion, or for the chemical reaction of the deposited material to form a coherent coating.

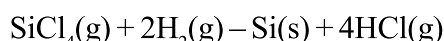
6.6 VAPOUR PHASE EPITAXY

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The main advantages of the Vapour Phase Epitaxy (VPE) are the ability to grow very good quality layers, with high growth rate (higher than μm min –1). Its principle is relatively simple and allows great flexibility (change in doping level or type of doping). In addition, the VPE can handle several large wafers, which is particularly desirable for photovoltaic applications. In this chapter, we introduce the principle of this method before discussing the theories and modelling for understanding the mechanisms governing the kinetics of crystal growth. It is followed by a detailed description of SiH_2Cl_2/H_2 system, well adapted to the growth of films for photovoltaic applications.

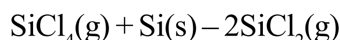
Vapour-Phase

Silicon is most commonly deposited by doping with silicon tetrachloride and hydrogen at approximately 1200 to 1250 °C



$$SiCl_4(g) + 2H_2(g) – Si(s) + 4HCl(g)$$

Where (g) and (s) represent gas and solid phases, respectively. This reaction is reversible, and the growth rate depends strongly upon the proportion of the two source gases. Growth rates above 2 micrometres per minute produce polycrystalline silicon, and negative growth rates (etching) may occur if too much hydrogen chloride byproduct is present. (In fact, hydrogen chloride may be added intentionally to etch the wafer.) An additional etching reaction competes with the deposition reaction:



$$SiCl_4(g) + Si(s) – 2SiCl_2(g)$$

Silicon VPE may also use silane, dichlorosilane, and trichlorosilane source gases. For instance, the silane reaction occurs at 650°C in this way:



$$SiH_4 – Si + 2H_2$$

This reaction does not inadvertently etch the wafer, and takes place at lower temperatures than deposition from silicon tetrachloride. However, it will form a polycrystalline film unless tightly controlled, and it allows oxidising species that leak into the reactor to contaminate the epitaxial layer with unwanted compounds such as silicon dioxide.

VPE is sometimes classified by the chemistry of the source gases, such as hydride VPE and metalorganic VPE.

Vapour-phase is used for thickening of a solid-phase crystallised silicon seed layer on glass. Cross-sectional transmission microscope images confirm that a transfer of crystallographic information has taken place from the seed layer into the epilayers. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy reveal that the density of planar defects (mainly on {111} plains) in the vapour-phase epitaxial sample is much higher than in the solid-phase epitaxial sample. These planar defects can act as recombination centres for free-

charge carriers. Consequently, PC1D modelled minority carrier diffusion length in the vapour-phase grown epilayer is 50% shorter than that in the solid-phase grown epilayer. As a result, a solar cell grown by solid-phase epitaxy achieves open circuit voltage of 468 mV, short circuit current of 9.17 mA/cm^2, and photovoltaic conversion efficiency at 2.75% which are all higher than those of the solar cell grown by vapour-phase epitaxy on the same seed layer, 400 mV, 7.28 mA/cm^2, 1.69%, respectively. It proves that solid-phase epitaxy is more suitable for the solar cell growth on the solid-phase crystallised silicon seed layer than vapour-phase epitaxy.

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6.7 EPITAXY OF COMPOUND SEMICONDUCTORS

Epitaxy is a method to grow or deposit monocrystalline films on a structure or surface. There are two types of epitaxy-homoepitaxy and heteroepitaxy. Homoepitaxy is a process in which a film is grown on a substrate of the same composition. Heteroepitaxy is a film that is grown on a substrate, which has a different composition.

Epitaxial silicon is grown using Vapour Phase Epitaxy (VPE). This is a modification of Chemical Vapour Deposition (CVD). Another technology, Molecular Beam Epitaxy (MBE), is mainly for compound semiconductors. MBE is a slow, line-of-sight technique, not suitable for filling trenches and other three-dimensional structures.

For silicon processes, epitaxy is used in source-drain and strain engineering techniques. They are also playing a big role in the channel in chip designs.

The big change in the channel took place at 90nm, when the industry introduced strain engineering in the region. Using a blanket epitaxial process, chipmakers integrated Silicon-Germanium (SiGe) stressors, or distortions in the crystal lattice, in PMOS transistors. This, in turn, boosted hole mobility and drive current.

Using the same epi process, chipmakers are moving towards strain engineering for the NMOS starting at 20nm. The NMOS transistors require a tensile strain, enabling a boost in drive current.

Still, today's strained-silicon technology is under stress. So, chipmakers may need to make a materials change in the channels at 10nm or 7nm. At one time, the leading candidate was Germanium (Ge) for PMOS and Indium-Gallium Arsenide (InGaAs) for NMOS. (Ge has an electron mobility of 3,900cm-square-over-Vs, compared to 1,500cm-square-over-Vs for silicon. InGaAs has an electron mobility of 40,000cm-square-over-Vs.)

Ge and III-V are fast but difficult to implement due to the lattice mismatch with silicon. Now, the industry is looking at a simpler approach. Chipmakers will

likely use SiGe for PMOS at 10nm or 7nm, depending on the company and requirements. For NMOS, the industry may stick with tensile silicon.

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In any case, there are two main approaches in terms of depositing Ge, SiGe or III-V materials in the channels–blanket and selective epi. The blanket approach calls for the epi materials to be grown everywhere on the surface. In selective, the epi materials are only grown on a select part of the surface.

At present, some prefer the traditional blanket approach. The blanket approach has some drawbacks, however. With blanket epi, a chipmaker may end up depositing materials on unwanted regions. In that case, the IC vendor must etch away those materials. All told, blanket epi may have more process steps, possibly making it more expensive.

For that reason, selective epi is also viable. In selective, a tool can mix and match materials with other types of materials. But in some respects, it is far more complex than blanket epi.

Imec, for one, has demonstrated a selective growth process, depositing germanium and InGaAs pillars into patterned oxide trenches to make a 'Virtual Substrate' for device fabrication. Using this technique, Imec demonstrated what it believes to be the first III-V finFETs integrated epitaxially on 300mm silicon wafers.

Imec's process starts by using standard shallow trench isolation processes to create a template, with pillars of silicon surrounded by silicon dioxide. Then, a silicon dioxide cap is deposited over the areas where InGaAs will ultimately go. In the uncapped regions, the silicon pillars are etched away, and the exposed trenches filled with germanium. Next, the germanium is capped with silicon dioxide and the InGaAs areas are exposed.

InGaAs pillar formation begins by etching out the silicon pillars to create a concave bottom surface, slightly wider than the ultimate trench width. Successive depositions of germanium, InP, and InGaAs follow, gradually accommodating the lattice mismatch between silicon and InGaAs. The narrow trenches are key to this process: because of the rounded bottom surface, dislocations tend to form at an angle to the sides of the trench, and are trapped against the sidewalls rather than propagating through the InP and InGaAs bulk. An active layer with acceptable quality is achieved with a thinner, less time-consuming deposition. Moreover, with selective deposition there is no need to etch InGaAs, or to dispose of toxic arsenic-based etch by-products.

6.8 APPLICATIONS

Epitaxy is used in nanotechnology and in semiconductor fabrication. Indeed, epitaxy is the only affordable method of high quality crystal growth for many semiconductor materials. In surface science, epitaxy is used to create and study monolayer and multilayer films of adsorbed organic molecules on single crystalline surfaces. Adsorbed molecules form ordered structures on atomically flat terraces of single

crystalline surfaces and can directly be observed via scanning tunnelling microscopy. In contrast, surface defects and their geometry have significant influence on the adsorption of organic molecules.

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Germanium is a key material in modern material science and society: it is used as a dopant in fibre optic glasses and in semiconductor devices, both in activating conduction in layers and also as a substrate for III–V epitaxy. Ge is also widely used in Infrared (IR) detection and imaging and as a polymerisation catalyst for Polyethylene Terephthalate (PET). Moreover, high-speed electronics for cell phone communications relies heavily on SiGe alloys. Ge electronics is nowadays gaining new interest because of the enhanced electronic properties of this material compared to standard silicon devices, but the lack of a suitable gate oxide still limits its development. High efficiency solar cells, mainly for space use but also for terrestrial solar concentration have surpassed 40% efficiency and Ge has a lead role in achieving this goal.

Molecular Beam Epitaxy: Materials and Applications for Electronics and Optoelectronics is presented in five parts: Fundamentals of MBE; MBE technology for electronic devices application; MBE for optoelectronic devices; Magnetic semiconductors and spintronics devices; and Challenge of MBE to new materials and new researches. The book offers chapters covering the history of MBE; principles of MBE and fundamental mechanism of MBE growth; migration enhanced epitaxy and its application.

Epitaxy, the process of growing a crystal of a particular orientation on top of another crystal, where the orientation is determined by the underlying crystal. The creation of various layers in semiconductor wafers, such as those used in integrated circuits, is a typical application for the process. In addition, epitaxy is often used to fabricate optoelectronic devices.

The commercial importance of epitaxy comes mostly from its use in the growth of semiconductor materials for forming layers and quantum wells in electronic and photonic devices, for example, in computer, video display, and telecommunications applications. The process of epitaxy is general, however, and so can occur for other classes of materials, such as metals and oxides, which have been used since the 1980s to create materials that display giant magnetoresistance (a property that has been used to produce higher-density digital storage devices).

In vapour phase epitaxy the deposition atoms come from a vapour, so that growth occurs at the interface between gaseous and solid phases of matter. Examples include growth from thermally vapourised material such as silicon or from gases such as silane (SiH_4), which reacts with a hot surface to leave behind the silicon atoms and to release the hydrogen back into the gaseous phase. In liquid phase epitaxy layers grow from a liquid source (such as silicon doped with small amounts of another element) at a liquid-solid interface. In solid phase epitaxy a thin amorphous (noncrystalline) film layer is first deposited on a crystalline substrate, which is then heated to convert the film into a crystalline layer. The epitaxial growth

then proceeds by a layer-by-layer process in the solid phase through atomic motion during the recrystallisation at the crystal-amorphous interface.

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Check Your Progress

1. Define the term epitaxy.
2. Explain about the homo-epitaxy growth.
3. What is the lattice misfit?
4. Define the liquid phase epitaxy.
5. Write the main advantages of vapour phase epitaxy.
6. Write the uses of epitaxial silicon.
7. Explain the commercial importance of epitaxy.

6.9 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Epitaxy (epi means 'Upon' and taxis means 'Ordered') is a term applied to processes that are used to grow a thin crystalline layer (film) on a crystalline substrate. The seed crystal in epitaxial processes is used as the substrate.
2. In this kind of growth the epitaxial layer and substrate are of the same material. For example- the Chemical vapour deposition of a single-crystal silicon thin film on a single-crystal silicon substrate having the same crystallographic orientation hence the process is known as homoepitaxy, which is accomplished by hydrogen reduction of dichlorosilane vapour.
3. The situation when two materials having different lattice constants are brought together by deposition of the layer of one material on top of the second. The lattice mismatch prevents the growth of defect-free epitaxial film unless the thickness in the thin film is below a certain critical thickness. The Lattice Constant of a semiconductor is described by the atomic spacing (in Angstroms) in the semiconductor crystal of that material.
4. The threshold current values of the best DWhat ouble Hetero structure (DH) MBE lasers are typically compared to LPE results. There are many variants of the LPE process, but in this approach most common to multilayer film growth a graphite holder used to slides a sample between materials melts of different compositions.
5. The main advantages of the Vapour Phase Epitaxy (VPE) are the ability to grow very good quality layers, with high growth rate (higher than ìm min^{-1}). Its principle is relatively simple and allows great flexibility (change in doping level or type of doping).

6. Epitaxial silicon is grown using Vapour-Phase Epitaxy (VPE). This is a modification of Chemical Vapour Deposition (CVD). Another technology, Molecular Beam Epitaxy (MBE), is mainly for compound semiconductors. MBE is a slow, line-of-sight technique, not suitable for filling trenches and other three-dimensional structures. For silicon processes, epitaxy is used in source-drain and strain engineering techniques. They are also playing a big role in the channel in chip designs.
7. The commercial importance of epitaxy comes mostly from its use in the growth of semiconductor materials for forming layers and quantum wells in electronic and photonic devices, for example, in computer, video display, and telecommunications applications. The process of epitaxy is general, however, and so can occur for other classes of materials, such as metals and oxides, which have been used since the 1980s to create materials that display giant magnetoresistance.

6.10 SUMMARY

- Epitaxy (epi means "upon" and taxis means "ordered") is a term applied to processes that are used to grow a thin crystalline layer (film) on a crystalline substrate.
- Process of heteroepitaxy, the crystal structures of the layer and the substrate must be similar to attain good crystalline integrity. The performance of many devices, such as CMOS(Complementary MOS) and DRAM (Dynamic Random Access Memory), can Films by Epitaxy Thin be enhanced by employing epitaxial wafers.
- Growth the epitaxial layer and substrate are of the same material. For example- the Chemical vapour deposition of a single-crystal silicon thin film on a single-crystal silicon substrate having the same crystallographic orientation hence the process is known as homoepitaxy, which is accomplished by hydrogen reduction of dichlorosilane vapour.
- The situation when two materials having different lattice constants are brought together by deposition of the layer of one material on top of the second.
- The lattice mismatch prevents the growth of defect-free epitaxial film unless the thickness in the thin film is below a certain critical thickness. The Lattice Constant of a semiconductor is described by the atomic spacing (in Angstroms) in the semiconductor crystal of that material.
- If the lattice constants are significantly different from each other, the mismatching atomic positions in the crystal at the boundaries can cause strain, resulting in cracks or dislocations that generally propagate through the structure.
- Historically, in the early age of technology, compound semiconductor growth was performed by using liquid phase epitaxial techniques and to date,

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numerous optoelectronic devices are still fabricated by using the same process.

- The threshold current values of the best Double Heterostructure (DH) MBE lasers are typically compared to LPE results. There are many variants of the LPE process, but in this approach most common to multilayer film growth a graphite holder used to slides a sample between materials melts of different compositions.
- Film growth obtained from the controlled cooling of the supersaturated melt. Different bins are required for each layer of different alloy composition.
- LPE is mainly applied for the thermally-controlled overgrowth of single-crystalline thin films using compound semiconductors and magnetic garnets from the melt on the top of the single-crystal substrate.
- The main advantages of the vapour phase epitaxy (VPE) are the ability to grow very good quality layers, with high growth rate (higher than ìm min – 1). Its principle is relatively simple and allows great flexibility (change in doping level or type of doping).
- Vapour-phase is used for thickening of a solid-phase crystallised silicon seed layer on glass. Cross-sectional transmission microscope images confirm that a transfer of crystallographic information has taken place from the seed layer into the epilayers.
- X-ray diffraction, scanning electron microscopy, and transmission electron microscopy reveal that the density of planar defects (mainly on {111} plains) in the vapour-phase epitaxial sample is much higher than in the solid-phase epitaxial sample.
- Epitaxy is a method to grow or deposit monocrystalline films on a structure or surface. There are two types of epitaxy-homoepitaxy and heteroepitaxy.
- Epitaxial silicon is grown using Vapour-Phase Epitaxy (VPE). This is a modification of Chemical Vapour Deposition (CVD). Another technology, molecularbeam epitaxy (MBE), is mainly for compound semiconductors. MBE is a slow, line-of-sight technique, not suitable for filling trenches and other three-dimensional structures.
- There are two main approaches in terms of depositing Ge, SiGe or III-V materials in the channels–blanket and selective epi. The blanket approach calls for the epi materials to be grown everywhere on the surface. In selective, the epi materials are only grown on a select part of the surface.
- Epitaxy is used in nanotechnology and in semiconductor fabrication. Indeed, epitaxy is the only affordable method of high quality crystal growth for many semiconductor materials. In surface science, epitaxy is used to create and study monolayer and multilayer films of adsorbed organic molecules on single crystalline surfaces.

- Germanium is a key material in modern material science and society: it is used as a dopant in fibre optic glasses and in semiconductor devices, both in activating conduction in layers and also as a substrate for III–V epitaxy.
- Materials and Applications for Electronics and Optoelectronics is presented in five parts: Fundamentals of MBE; MBE technology for electronic devices application; MBE for optoelectronic devices; Magnetic semiconductors and spintronic devices; and Challenge of MBE to new materials and new researches.
- Epitaxy, the process of growing a crystal of a particular orientation on top of another crystal, where the orientation is determined by the underlying crystal.

6.11 KEY WORDS

- **Epitaxy:** Epitaxy (epi means 'Upon' and taxis means 'Ordered') is a term applied to processes that are used to grow a thin crystalline layer (film) on a crystalline substrate. The seed crystal in epitaxial processes is used as the substrate.
- **Hetero-epitaxy growth:** In this kind of growth the epitaxial layer and the substrate both are of a different material.
- **Lattice misfit:** when two materials having different lattice constants are brought together by deposition of the layer of one material on top of the second. The lattice mismatch prevents the growth of defect-free epitaxial film unless the thickness in the thin film is below a certain critical thickness.
- **Vapour Phase Epitaxy (VPE):** Vapour Phase Epitaxy (VPE) are the ability to grow very good quality layers, with high growth rate (higher than ìm min –1). Its principle is relatively simple and allows great flexibility (change in doping level or type of doping).
- **Molecular beam epitaxy:** Materials and Applications for Electronics and Optoelectronics is presented in five parts: Fundamentals of MBE; MBE technology for electronic devices application; MBE for optoelectronic devices; Magnetic semiconductors and spintronics devices; and Challenge of MBE to new materials and new researches.

6.12 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the epitaxy.
2. Illustrate the structural aspects of epitaxy.

3. Write the short notes on lattice misfit and imperfections.
4. What do you mean by liquid phase epitaxy?
5. Analyse the epitaxy of compound semiconductor.
6. Write the applications of epitaxy.

Long-Answer Questions

1. Discuss briefly the concept of epitaxy with the help of examples.
2. Explain the structural aspects of epitaxy with the help of appropriate examples.
3. Briefly explain the significance of lattice misfit and imperfections.
4. Describe the liquid phase epitaxy with the help of examples.
5. Explain about the epitaxy of compound semiconductors giving examples.
6. Briefly explain the applications of epitaxy.

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BLOCK - III
OPTICAL MATERIALS

NOTES

UNIT 7 PRINCIPLES OF LASER

Structure

7.0 INTRODUCTION

A Laser is a device that emits light through a process of optical amplification based on the stimulated emission of electromagnetic radiation. The abbreviation LASER stands for 'Light Amplification by Stimulated Emission of Radiation'. The first Laser was built in 1960 by Theodore H. Maiman at Hughes Research Laboratories, based on theoretical work by Charles Hard Townes and Arthur Leonard Schawlow. A Laser differs from other sources of light in that it emits light which is coherent. Spatial coherence allows a Laser to be focused to a tight spot, enabling applications, such as Laser cutting and lithography. Spatial coherence also allows a Laser beam to stay narrow over great distances (collimation), enabling applications, such as Laser pointers and lidar. Lasers can also have high temporal coherence, which allows them to emit light with a very narrow spectrum, i.e., they can emit a single colour of light. Alternatively, temporal coherence can be used to produce pulses of light with a broad spectrum but durations as short as a femtosecond ('Ultrashort Pulses'). Lasers are used in optical disk drives, Laser printers, barcode scanners, DNA sequencing instruments, fiber-optic, semiconducting chip manufacturing (photolithography), and free-space optical communication, Laser surgery and skin treatments, cutting and welding materials, military and law enforcement devices for marking targets and measuring range and speed, and in Laser lighting displays for entertainment. They have been used for car headlamps on luxury cars, by using a Blue Laser and a phosphor to produce highly directional white light. In 1917, Einstein start an era by starting basic concept for Laser which is well know the phenomena of stimulated emission, when a photon let to interacts with molecule in excited state or atom resulting an emission of a second photon having frequency,

phase, polarisation, and direction. The precursor of the Laser is called the MASER, full form of MASER is 'Microwave Amplification by Stimulated Emission of Radiation'. Meaning of MASER was developed by Charles Townes and Jim Gordon in Russia by Nicolay Basov and Alexsandr Prokhorov in 1954 at Columbia University. These masers made by ammonia were based on two-energy-level gaseous systems that could eternally sustain process of population inversion. It was 1956 when Nicolaas Bloembergen introduced the concept of a three-level solid-state MASER at Harvard, which was explained by researchers at Bell Labs.

For the normal population of atoms, there will always be more atoms in the lower energy levels than in the upper levels. Because the probability for an individual atom to absorb a photon is the same as the probability for an excited atom to emit a photon through stimulated emission, the collection of real atoms shall be a net absorber, not a net emitter, and amplification will not be possible. Accordingly, to make a laser, we have to create a 'Population Inversion.'

The optical cavities (The arrangement to make back and forth the photons) are made to amplify the light within the cavity having lasing medium, the highly reflective mirrors used to reflect back photon. Q-switching is a simple and most convenient concept. The energy stored during the process of population inversion up to a threshold level and then suddenly it is released quickly in the form of a huge pulse. Mode-locking is defined as the process by virtue of which a Laser can produce very short duration pulses of light of the order of picoseconds (10^{-12} s) or femtoseconds (10^{-15} s). Hence a Laser operating in this range of output termed as femtosecond Laser.

In this unit, you will study about the basic principle of Laser, population inversion in three and four level system, resonators, Q-switching and mode locking.

7.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss about the principle of Laser
- Explain about the population inversion
- Introduces of resonators
- Illustrate the Q-switching and mode locking

7.2 PRINCIPLES OF LASER

In 1917, Einstein start an era by starting basic concept for Laser which is well know the phenomena of stimulated emission; when a photon let to interacts with molecule in excited state or atom resulting an emission of a second photon having frequency, phase, polarisation, and direction. The abbreviation LASER stands for 'Light Amplification by Stimulated Emission of Radiation'. The precursor of

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Fig. 7.1 *Charles Townes and Arthur Schawlow*

Just after the discovery of maser, Arthur Schawlow and Charles Townes started to work on masers that can operate to give infrared or visible light. In this journey Schawlow and Townes invent an optical cavity by adjusting two highly reflecting mirrors which are placed parallel to each other and able to keeping the amplifying of light into medium in 1957. After this in 1958, they successfully write a seminal Physical Review paper on their inventions and patent application was submitted by them for the so-called optical maser. This lengthy Physical Review article get publicity and was mostly read in the United States America which create huge interest among other researchers working in this field, especially on experimentalists who were attempting to build the first Laser system. Despite of this article rightfully gave Schawlow and Townes invented the Laser system, and after their work many others research groups came with the same concept of 'Open Cavity'. Gordon Gould also proposes a concept of open cavity when he was only a graduate student at Columbia University. Gould was the first inventor who publically used the word Laser, for 'Light Amplification by Stimulated Emission of Radiation' at the June 1959 Ann Arbor Optical Pumping Conference.

Theodore Maiman also invent the first working Laser system at Hughes Research Lab in 1960 in his paper he explained the operation of this Laser which was published in Nature three months, later of invention. Afterward, more than 55,000 researcher used the concept of the Laser have been granted in the United States. Nowadays, Laser system we use and read its applications are the results of not only a individual's efforts, but it contains the work of many famous scientists and engineers who were pioneer at that time in optics and photonics. Charles Townes was among these such a prominent mind working at Columbia University,

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who invented the maser which ultimately precursor to the Laser system later, and then Arthur Schawlow at Bell Laboratories, who along with Townes published theoretical research paper in 1958 that helped to conduct further the improvement of the Laser and who jointly were awarded the first Laser patent in 1960.



Fig. 7.2 *Dr. Theodore Maiman of Hughes Research Laboratories, with the First Working Laser. Photo Credit: HRL Laboratories, LLC*

Maiman's advanced Laser used a powerful energy source to excite atoms in a synthetic Ruby to higher energy levels. At a fixed energy level, some atoms emitted particles of light called photons. These newly created photons collide with other atoms, rapidly stimulating the emission of more same photons and amplifying the light intensity. Maiman was able to continue the process of stimulated emission and amplification by placing a completely reflecting silver mirror on one end of the model and a partially reflecting silver mirror on the other end. This setup allows photons to bounce back and forth between the mirrors until they gained enough intensity to burst through the partially silvered end as a powerful, coherent, beam of light—what you can today find on the behalf of a Laser pointer.

7.3 POPULATION INVERSION IN THREE LEVEL AND FOUR LEVEL SYSTEMS

Population

The number of atoms per unit volume in an energy level is the population of that level. According to Boltzmann principle, at thermal equilibrium the relative population between any two energy levels is given by

$$\frac{N_2}{N_1} = \exp\left[\frac{E}{K_B T}\right] \qquad \dots (7.1)$$

Where N_1 and N_2 are the populations of the lower and upper energy states respectively, T is the temperature, and k the Boltzmann constant. The above equation states that the number of atoms in the ground state is more than in the higher states i.e. the population of ground state is maximum but decreases exponentially as energy level decreases as shown in Figure 7.3.

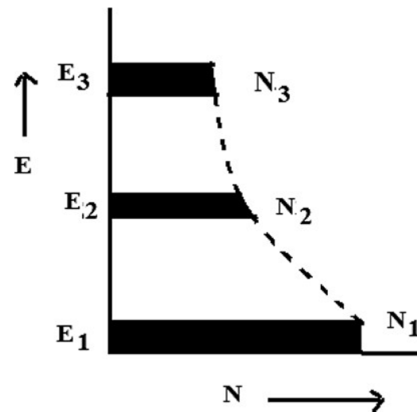


Fig. 7.3 *Energy State Diagram of Population Inversion*

Population Inversion

Consider two energy states, a ground energy state E_1 and excited enegystate E_2. Normally the number of atoms in the ground state is more than in the higher states. Lasing mechanism requires exclusively stimulated emission to occur. This will be done when the number of atoms in excited state is more than in the ground state. When the population of E_2 and E_1 gets inverted, this condition is called as population inversion.

Pumping

To achieve population inversion it is necessary that the atoms in the ground state be continuously transferred to excited state. The mechanism of raising ground state atoms to upper states is known as **pumping**. To raise atoms from ground state to upper states input energy is required. In solid state Lasers and dye Lasers **optical pumping** is used whereas **electron pumping** method is employed in gas Lasers and in semiconductor Lasers. Two important pumping schemes are widely used. They are

A.Three-Level Pumping Scheme

Consider an atomic system having three energy states, E_1 is ground state also called as lower lasing level, E_2 and E_3 are excited states. Energy state E_2 is metastable state and also called as upper lasing level and E_3 is uppermost, unstable state. The ground state atoms are pumped to unstable state E_3 when light of energy $hJ = E_3 - E_1$ is incident on them. Since it is unstable state the excited atoms at this state make spontaneous downward transition to matastable state E_2. This transition is non-radiative. In metastable state atoms reside for longer time. The pumping

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continues and after some time there will be large number of atoms accumulated at E_2 state. When more than half of the ground state atoms gather at E_2, a state of population inversion is achieved between E_1 and E_2. Now a photon of energy $hJ = E_2 - E_1$ released in the spontaneous transition, causes stimulated emission.

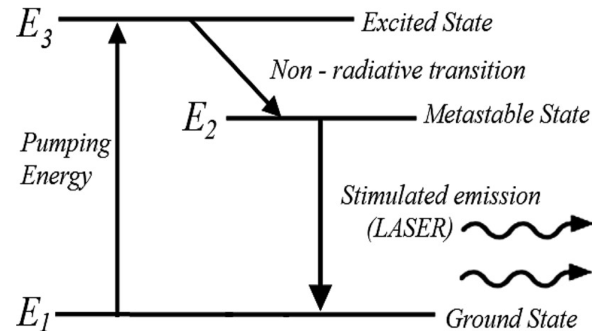


Fig. 7.4 *Three Level Pumping Scheme*

In three-level Laser system to pump more than half of the ground state atoms to the upper state a very high energy is required. This scheme produces light only in pulses

B. Four-Level Pumping Scheme

In four-level pumping scheme, E_1 is ground energy state, E_2 is lower lasing level, E_3 is metastable state, E_4 is the pumping state. Atoms are pumped from ground state to the uppermost level E_4 by light. Since E_4 is unstable state, the atoms quickly drop to energy state E_3 which is the metastable state. The population at this state grows rapidly. The energy state E_2 is virtually empty, as at normal temperature the atoms can't jump to it by thermal energy. Hence population inversion is achieved between E_3 and E_2. A photon of energy $hJ = E_3 - E_2$ emitted spontaneously can start

Stimulated emission bringing the atoms to the state E_2 rather than at the ground state. From E_2 the atom make non-radiative transition very fast to the ground state. This scheme operates in continuous wave mode.

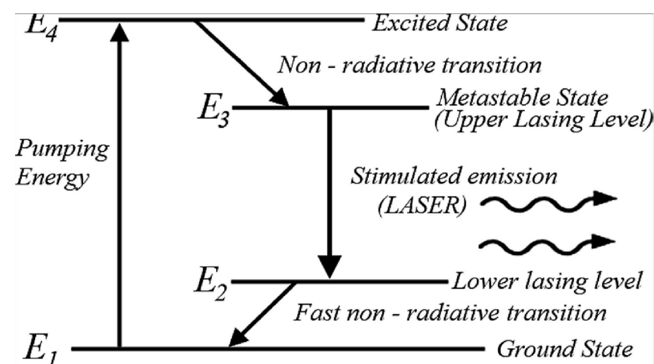


Fig. 7.5 *Four Level Pumping Scheme*

7.4 RESONATORS, Q-SWITCHING AND MODE LOCKING

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Resonators

The optical cavities (The arrangement to make back and forth the photons) are made to amplify the light within the cavity having lasing medium, the highly reflective mirrors used to reflect back photon. The light enters the cavity through one mirror, reflects back from the opposite mirror, and again returns back to the first mirror, but some of photons is transmitted through each mirror as no mirror is perfectly reflecting. This light transmitted by the first mirror in each arm is the light which obstructs the beam splitter to produce the signal.

There are numerous kinds of optical resonators. The cavity is perfectly maintained in such configuration that the beam will remain entirely within the cavity's mirrors during amplification process in lasing medium. These are made to as obey where R_1 and R_2 are the radii of curvature of the mirrors and L is the distance between the mirrors:

(a) Plane-parallel $R_1 = R_2 = \infty$

(b) Concentric (spherical) $R_1 + R_2 = L$

(c) Confocal $R_1 + R_2 = 2L$

(d) Hemispherical $R_1 = L$, $R_2 = \infty$

(e) Concave-convex $R_1 >> L$, $R_2 = L - R_1$

Basically there are five types of stable optical cavities, as exhibited in Figure. These types of resonators have different parameters such as focal lengths of the mirrors (governed by the mirror's radius of curvature) and in their distance between the mirrors (cavity length). As we can see from Figure 7.6, some photons beams have different directions within the cavity and a particular cavity is chosen for a variety of purposes.

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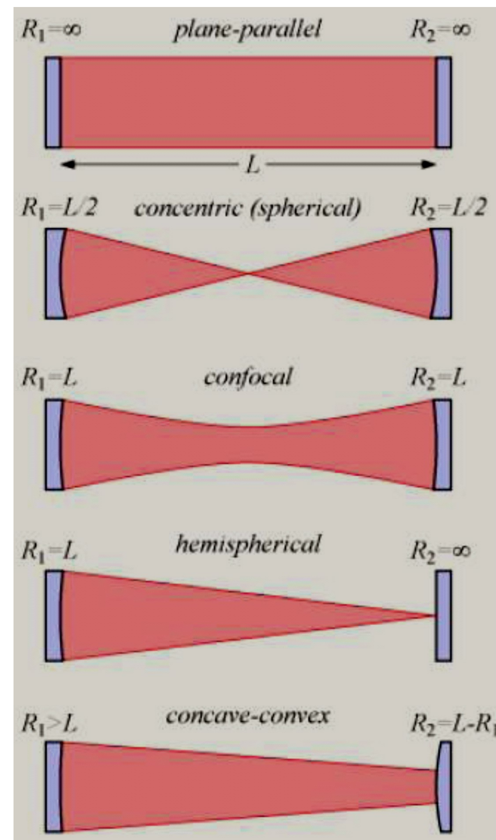


Fig. 7.6 *Five Types of Stable Cavities*

There is simplest mathematical equation which can be used to know that whether a particular cavity is stable or not. The rule for predicting about that cavity is stable or not can be stated as follows in simplest form:

For a cavity made of two spherical mirrors (of radii of curvature R_1 and R_2) separated by a distance L, the cavity is stable if

$$0 \leq g_1 g_2 \leq 1$$

Where,

$$g_1 = 1 - \frac{L}{R_1}$$

$$g_2 = 1 - \frac{L}{R_2}$$

Q-Switching

Q-switching is a simple and most convenient concept. The energy stored during the process of population inversion up to a threshold level and then suddenly it is released quickly in the form of a huge pulse. This is similar to storing water in a tank with a hole with a softly fitted cork in the bottom as the water level and hence

weight rise in the tank the cork suddenly pushed out at a certain weight resulting in releasing of all water rapidly. The Q defines the quality for a particular type of the resonator. A resonator having high-Q possess high-quality or in other words it has a low loss. The resonator having any blocked mirror cannot have very high-Q. When the mirror is immediately unblocked, the Q-factor is switched from low value to high value. Q-switched Laser is the Laser whose resonator can be switched from low quality to high quality and vice versa. Since Lasers pulses are useful in many types of technical applications where Continuous-Wave (CW) Lasers not able to give satisfactory work due to their low energy output relatively. The energy of a pulsed Laser is tightly packed into tiny concentrated packages which are more powerful than the normal-strength energy that comes from the output of a continuous-wave Laser.

Q-switching is a process for obtaining energetic short (but not ultra short) pulses from a Laser by modulating the intra-cavity losses and thus the **Q** factor of the Laser resonator. The process of Q switching is generally applied for the production of nanosecond pulses of high energy and peak power with solid-state bulk Lasers. Q-switching is a technique used mostly exclusively with optically pumped, solid-state Lasers.

Types of Q-Switches

A straight forward process to Q-switching a Laser is making a beam block in front of the Laser mirror, but it is not so practical. But the main problem is about the beam to block completely. Let's assume a beam of 0.5 mm in diameter and then block must be pulled out few nanoseconds time, the block must need to be throwing out using a velocity which is greater than the speed of sound and practically which is not very easy to arrange. Hence keeping all these basic concepts in mind there are generally four types of Q-switches that are commonly used in Lasers are:

1. Mechanical Q-switches move something—using a mirror—to switch the resonator Q.
2. Acousto-Optic (AO) and in this point electro-optic (E-O)- Q-switches where diffracted part of the Laser beam passing through them to eliminate feedback from a resonator mirror. The polarisation of light passing through an Electro-Optic (E-O) Q-switch can rotate so that a polariser prevents light from returning from the mirror.
3. Dye Q-switch where dye is used to absorbs light traveling towards the mirror until the intensity of the light becomes high enough to bleaches the dye, allowing later light to pass through after bleaching dye , the Q-switch and reach the mirror.

Mode Locking

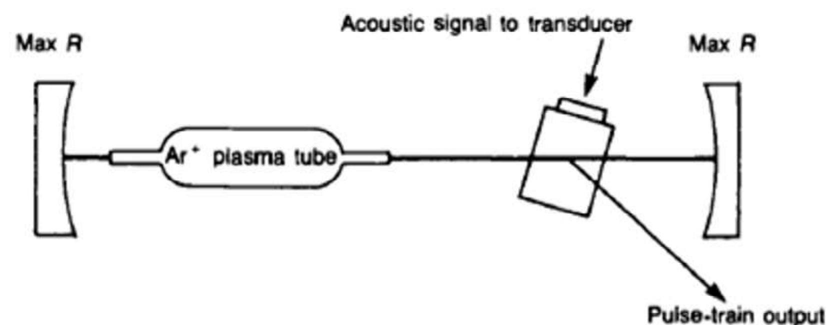
The pulsed output having high intensity from a Laser can be obtained from by Q-switching, but this process of lasing not properly work in the Lasers having

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very short lifetime of upper-state to store sufficient energy for output. Mode-locking is defined as the process by virtue of which a Laser can produce very short duration pulses of light of the order of picoseconds (10^{-12} s) or femtoseconds (10^{-15} s). hence a Laser operating in this range of output termed as femtosecond Laser.

Mode Locking: Time Domain

A mode locked Laser is shown in Figure 7.7 having the optical energy between the mirrors has been reduced to a very short pulse in such a way it is shorter than the resonator energy. In Q-switched or a cavity-dumped Laser, the whole resonator is filled completely with the energy while in a mode locked Laser, the energy is first converted into a pulse that travel back and forth between two mirrors. Every time this intracavity pulse rebound off from the mirror which is partially transmitting and an output pulse is transmitted throughout that mirror. The energy is compressed into the mode locked pulse inside the resonator by using a mode locking modulator, which is basically a fast optical gate (e.g., it could be an E-O Q-switch). The gate made to opens once per round-trip transit time, letting the pulse through while for the remaining time the gate is kept closed; the only mode locked pulse light can oscillate between two mirrors. This mode locking modulator is placed as close as possible to the mirror and it made to opens only once while the pulse passes through it, reflects off the mirror, and passes through the mode locking modulator again. The average power of Laser beam is not affected by mode-locking. The output of a modelocked Laser is in the form of a train of short pulses. The time separation is defined as the distance traveled by the intracavity pulse between two successive reflections from the output mirror divided by its velocity. The period between pulses is given by $2L/c$, where L is again the optical distance between the mirrors of cavity. While the frequency of a modelocked pulses of light is the reciprocal of the period, or f= $cl2L$. If a Laser whose mirrors are separated by a distance of 30 cm shall produce a modelocked pulse train at 500 megahertz MHz—500 million pulses of light per second.



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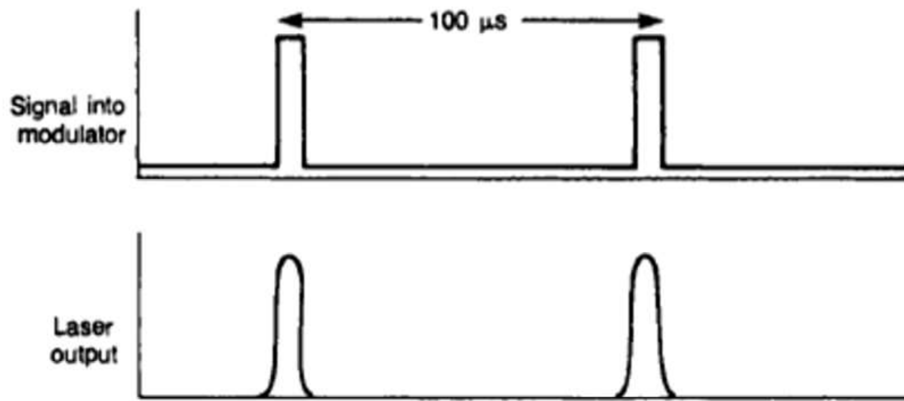


Fig. 7.7 *Mode Locking Laser*

Mode Locking: Frequency Domain

A Laser has three longitudinal modes which are oscillating simultaneously, as shown in Figure7.8. The waves that are moving inside the Laser resonator having the speed of light only show how it looks like at one place in time. Most places in the Laser cavity will be like the point A shown in Figure 7.8: the three modes add up together resulting into a very small total light intensity as they interfere with each other destructively. But at one (or maybe more) place inside the Laser cavity, where all modes interfere constructively and produce maximums as they got add up.

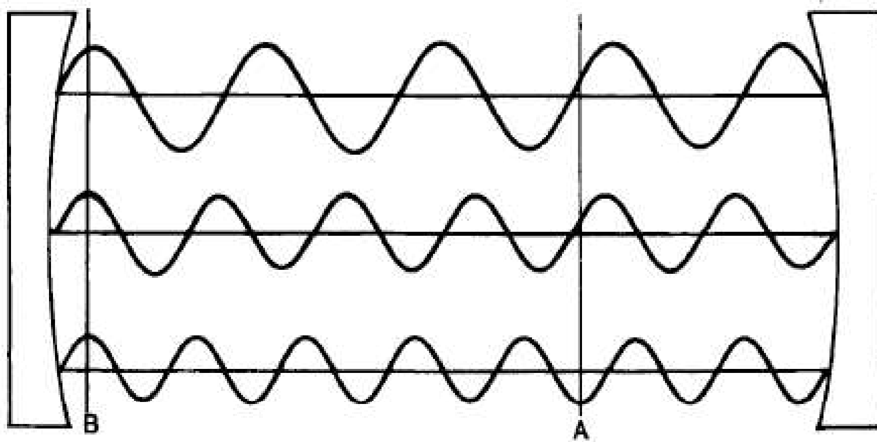


Fig. 7.8 *Three Longitudinal Modes are shown Spatially Displaced for Clarity. The Three Modes add Constructively at A*

All the three waves from three modes having speed equal to that of speed of light at point where they add up constructively to give maximum. As here already shown, constructive interference at this particular spot creates the modelocked pulse. But main problem is that in case of a free-running Laser—one that's not

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modelocked—the three modes will not stay in phase with each other as shown in Figure 7.8. Because of perturbations induced by Resonator, some of these modes stop oscillating and eventually when they start oscillating again, they will oscillate with different phase. So it is essential to lock modes together in same phase to produce a modelocked pulse at Laser output.

Application of Mode Locking

Generally the Modelocked Lasers do not have very high power pulses. These pulses are very short duration, but also many of them very small energy. Thus, modelocked Lasers without amplification are not having practical applications because it needs high peak powers. Modelocked Lasers are generally utilized where very short pulses are required. A modelocked pulse after transmission is reflected by a far object like a satellite and the total travel to the transmitter is measured with accuracy. As the Laser pulse moves with the speed of light hence the distance of that object can be calculated accurately. Due to their several meters long pulses, the accuracy of a Q-switched Laser-ranging instrument is not much better than a meter. However, if the pulse from a modelocked Laser is only several centimeters long in that case Laser-ranging system can be used with much greater accuracy. Modelocked Lasers can be used as spectroscopic tools to explore very fast phenomena. Spectroscopy is a complete science which involves analysis of matter by observing of interaction of light and matter. If the matter under analysis changes very quickly or says in a fraction of a nanosecond, then the fast instrument is required for its accurate analysis. The short pulse beam produced by a modelocked Laser is one among the few tools that can be used to investigate the chemical or physical reactions which is very fast.

Check Your Progress

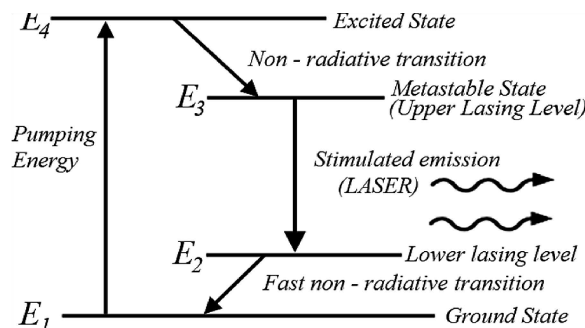
1. Explain the principles of Laser.
2. Define the population inversion in three level systems.
3. Illustrate the population inversion in four level systems.
4. Elaborate on the resonators.
5. Analyse the Q-switching.
6. State the mode locking.

7.5 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Laser which is well know the phenomena of stimulated emission; when a photon let to interacts with molecule in excited state or atom resulting an emission of a second photon having frequency, phase, polarisation, and direction. The abbreviation LASER stands for 'Light Amplification by Stimulated Emission of Radiation'.

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2. An atomic system having three energy states, E_1 is ground state also called as lower lasing level, E_2 and E_3 are excited states. Energy state E_2 is metastable state and also called as upper lasing level and E_3 is uppermost, unstable state.
3. Stimulated emission bringing the atoms to the state E_2 rather than at the ground state. From E_2 the atom make non-radiative transition very fast to the ground state. This scheme operates in continuous wave mode.



4. The optical cavities (The arrangement to make back and forth the photons) are made to amplify the light within the cavity having lasing medium, the highly reflective mirrors used to reflect back photon. The light enters the cavity through one mirror, reflects back from the opposite mirror, and again returns back to the first mirror, but some of photons is transmitted through each mirror as no mirror is perfectly reflecting. This light transmitted by the first mirror in each arm is the light which obstructs the beam splitter to produce the signal.
5. Q switching is a process for obtaining energetic short (but not ultra short) pulses from a Laser by modulating the intra-cavity losses and thus the **Q** factor of the Laser resonator. The process of Q switching is generally applied for the production of nanosecond pulses of high energy and peak power with solid-state bulk Lasers. Q-switching is a technique used mostly exclusively with optically pumped, solid-state Lasers.
6. The pulsed output having high intensity from a Laser can be obtained from by Q-switching, but this process of lasing not properly work in the Lasers having very short lifetime of upper-state to store sufficient energy for output. Mode-locking is defined as the process by virtue of which a Laser can produce very short duration pulses of light of the order of picoseconds (10^{-12} s) or femtoseconds (10^{-15} s). hence a Laser operating in this range of output termed as femtosecond Laser.

7.6 SUMMARY

- Laser which is well know the phenomena of stimulated emission; when a photon let to interacts with molecule in excited state or atom resulting an

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emission of a second photon having frequency, phase, polarisation, and direction. The abbreviation LASER stands for "Light Amplification by Stimulated Emission of Radiation".

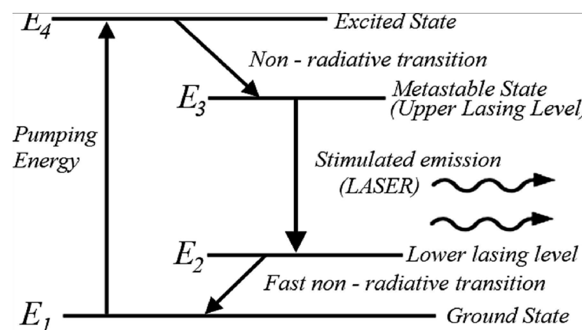
- Full form of MASER is 'Microwave Amplification by Stimulated Emission of Radiation'. Meaning of MASER was developed by Charles Townes and Jim Gordon in Russia by Nicolay Basov and Alexsandr Prokhorov in 1954 at Columbia University.
- Maiman's advanced Laser used a powerful energy source to excite atoms in a synthetic Ruby to higher energy levels. At a fixed energy level, some atoms emitted particles of light called photons.
- Stimulating the emission of more same photons and amplifying the light intensity. Maiman was able to continue the process of stimulated emission and amplification by placing a completely reflecting silver mirror on one end of the model and a partially reflecting silver mirror on the other end.
- The number of atoms per unit volume in an energy level is the population of that level. According to Boltzmann principle, at thermal equilibrium the relative population between any two energy levels is given by

$$\frac{N_2}{N_1} = \exp\left[\frac{E}{K_B T}\right]$$

- Consider two energy states, a ground energy state E_1 and excited enegystate E_2. Normally the number of atoms in the ground state is more than in the higher states. Lasing mechanism requires exclusively stimulated emission to occur. This will be done when the number of atoms in excited state is more than in the ground state. When the population of E_2 and E_1 gets inverted, this condition is called as population inversion.
- The mechanism of raising ground state atoms to upper states is known as pumping. To raise atoms from ground state to upper states input energy is required. In solid state Lasers and dye Lasers optical pumping is used whereas electron pumping method is employed in gas Lasers and in semiconductor Lasers. Two important pumping schemes are widely used.
- An atomic system having three energy states, E_1 is ground state also called as lower lasing level, E_2 and E_3 are excited states. Energy state E_2 is metastable state and also called as upper lasing level and E_3 is uppermost, unstable state.
- In four-level pumping scheme, E_1 is ground energy state, E_2 is lower lasing level, E_3 is metastable state, E_4 is the pumping state. Atoms are pumped from ground state to the uppermost level E_4 by light. Since E_4 is unstable state, the atoms quickly drop to energy state E_3 which is the metastable state.

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- The population at this state grows rapidly. The energy state E_2 is virtually empty, as at normal temperature the atoms can't jump to it by thermal energy. Hence population inversion is achieved between E_3 and E_2.
- Stimulated emission bringing the atoms to the state E_2 rather than at the ground state. From E_2 the atom make non-radiative transition very fast to the ground state. This scheme operates in continuous wave mode.



- The optical cavities (The arrangement to make back and forth the photons) are made to amplify the light within the cavity having lasing medium, the highly reflective mirrors used to reflect back photon. The light enters the cavity through one mirror, reflects back from the opposite mirror, and again returns back to the first mirror, but some of photons is transmitted through each mirror as no mirror is perfectly reflecting. This light transmitted by the first mirror in each arm is the light which obstructs the beam splitter to produce the signal.
- Basically there are five types of stable optical cavities, as exhibited in Figure. These types of resonators have different parameters such as focal lengths of the mirrors (governed by the mirror's radius of curvature) and in their distance between the mirrors (cavity length). As we can see from figure five types of stable cavities, some photons beams have different directions within the cavity and a particular cavity is chosen for a variety of purposes.
- Q-switching is a simple and most convenient concept. The energy stored during the process of population inversion up to a threshold level and then suddenly it is released quickly in the form of a huge pulse.
- Q switching is a process for obtaining energetic short (but not ultra short) pulses from a Laser by modulating the intra-cavity losses and thus the Q factor of the Laser resonator. The process of Q switching is generally applied for the production of nanosecond pulses of high energy and peak power with solid-state bulk Lasers. Q-switching is a technique used mostly exclusively with optically pumped, solid-state Lasers.
- Acousto-Optic (AO) - Q-switches where diffracted part of the Laser beam passing through them to eliminate feedback from a resonator mirror. The polarization of light passing through an Electro-Optic (E-O) Q-switch can rotate so that a polarizer prevents light from returning from the mirror.

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- The pulsed output having high intensity from a Laser can be obtained from by Q-switching, but this process of lasing not properly work in the Lasers having very short lifetime of upper-state to store sufficient energy for output. Mode-locking is defined as the process by virtue of which a Laser can produce very short duration pulses of light of the order of picoseconds (10^{-12} s) or femtoseconds (10^{-15} s). hence a Laser operating in this range of output termed as femtosecond Laser.
- In Q-switched or a cavity-dumped Laser, the whole resonator is filled completely with the energy while in a mode locked Laser, the energy is first converted into a pulse that travel back and forth between two mirrors.
- Generally the Modelocked Lasers do not have very high power pulses. These pulses are very short duration, but also many of them very small energy. Thus, modelocked Lasers without amplification are not having practical applications because it needs high peak powers.

7.7 KEY WORDS

- **Population:** The number of atoms per unit volume in an energy level is the population of that level. According to Boltzmann principle, at thermal equilibrium the relative population between any two energy levels is given by

$$\frac{N_2}{N_1} = \exp\left[\frac{E}{K_B T}\right]$$

- **Population inversion:** Consider two energy states, a ground energy state E_1 and excited enegystate E_2. Normally the number of atoms in the ground state is more than in the higher states. Lasing mechanism requires exclusively stimulated emission to occur. This will be done when the number of atoms in excited state is more than in the ground state. When the population of E_2 and E_1 gets inverted, this condition is called as population inversion.
- **Resonators:** The optical cavities (The arrangement to make back and forth the photons) are made to amplify the light within the cavity having lasing medium, the highly reflective mirrors used to reflect back photon. The light enters the cavity through one mirror, reflects back from the opposite mirror, and again returns back to the first mirror, but some of photons is transmitted through each mirror as no mirror is perfectly reflecting. This light transmitted by the first mirror in each arm is the light which obstructs the beam splitter to produce the signal.
- **Q switching** is a process for obtaining energetic short (but not ultra short) pulses from a Laser by modulating the intra-cavity losses and thus the Q factor of the Laser resonator. The process of Q switching is generally applied for the production of nanosecond pulses of high energy and peak

power with solid-state bulk Lasers. Q-switching is a technique used mostly exclusively with optically pumped, solid-state Lasers.

- **Mode locking:** The pulsed output having high intensity from a Laser can be obtained from by Q-switching, but this process of lasing not properly work in the Lasers having very short lifetime of upper-state to store sufficient energy for output. Mode-locking is defined as the process by virtue of which a Laser can produce very short duration pulses of light of the order of picoseconds (10^{-12} s) or femtoseconds (10^{-15} s). hence a Laser operating in this range of output termed as femtosecond Laser.

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7.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Explain about the state of Laser and its uses.
2. Define the population inversion.
3. Illustrate the three level pumping scheme of population inversion.
4. Give the advantages and disadvantages of Laser.
5. Explain the applications of Laser.
6. What are resonators?
7. Define the term Q-switching.
8. What is mode locking?

Long-Answer Questions

1. Explain briefly the principle of Laser.
2. Discuss in detail about the uses and types of Laser.
3. Brief a note on the population inversion of three level and four level with the help of energy state diagrams.
4. Briefly explain about the resonators giving appropriate examples.
5. Discuss briefly about the Q-switching and mode locking techniques giving appropriate examples.

7.9 FURTHER READINGS

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UNIT 8 TYPES OF LASER

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Structure

8.0 INTRODUCTION

There are many hundreds of Solid-State media in which Laser action has been achieved, but relatively few types are in widespread use. Of these, probably the most common is Neodymium-doped Yttrium Aluminium Garnet (Nd: YAG). Neodymium-doped Glass (Nd: Glass) and Ytterbium-doped Glasses or Ceramics are used at very high power levels (terawatts) and high energies (mega Joules), for multiple-beam inertial confinement fusion. The first material used for Lasers was synthetic Ruby crystals. Ruby Lasers are still used for a few applications, but they are not common because of their low power efficiencies. At room temperature, Ruby Lasers emit only short pulses of light, but at cryogenic temperatures they can be made to emit a continuous train of pulses.

Some Solid-State Lasers can also be tunable using several intracavity techniques, which employ etalons, prisms, and gratings, or a combination of these. Titanium-doped sapphire is widely used for its broad tuning range, 660 to 1080 nanometres. Alexandrite Lasers are tunable from 700 to 820 nm and yield higher-energy pulses than Titanium-Sapphire Lasers because of the gain medium's longer energy storage time and higher damage threshold.

Ruby Laser is in the family of solid state Lasers. This type of Laser was first designed by Maiman in 1960 and still used on a wide scale with high optical quality and the He-Ne Laser mixture of Helium (He) and Neon (Ne) is used as the Laser active medium. Here He atoms plays an important role for the excitation of the Ne atoms. The He-Ne Laser is excited by a stationary glow discharged by DC current. Eventually, Laser active metastable states are not present in He. The 3s and 2s bands are the two metastable states of Ne. Energy states 1s0 and 2s1

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of He are very close in height to the 3S and 2S states of Ne. Difference between them is about 200 cm^{-1} only. The Neodymium doped Yttrium Aluminium Garnet Laser is in the group of solid state Lasers. It is a four level Laser system having two most intense Lasers of wavelengths 1.0642 μm and 1.0615 μm (IR region). There are atomic energy levels in Neodymium (Nd) ion in Yttrium Aluminium Garnet (YAG) crystal. These five groups of states give rise to five spectral bands in the Nd: YAG absorption spectrum.

Among the semiconductors there are direct band and indirect band semi-conductors. In direct band semiconductors the recombination of an electron and a hole takes place directly thereby emitting photons. Hence used for Laser action.

Based on the number of semiconducting materials used in the fabrication of p-n Junctions, the semiconductor Lasers are classified as homojunction lasers and heterojuction Lasers.

In this unit, you will study about the solid state Laser, Ruby and Nd : YAG Laser, semiconductor Laser, GaAs/AlGaAs semiconductor Laser, Gas Laser, He-Ne and CO_2 Laser.

8.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss about the solid state Laser
- Explain working mechanism of Ruby and Nd : YAG Laser
- Introduces of semiconductor Laser
- Illustrate the Ga As/ Al Ga As semiconductor Laser
- Understand the gas Laser
- Describe the He-Ne and CO_2 Laser

8.2 SOLID STATE LASER

According to the state of Laser active material different types of Lasers are developed. Categorically we referred some of them.

Solid State Lasers: In this category, there are different types of Laser System e.g. Ruby Laser, Nd: YAG Laser, U^{+3} in CaF_2 Laser etc.

Dye Laser: Rhodamine 6G (Xanthene dye) Laser.

Gas Lasers: He-Ne (Helium-Neon) Laser, Ion Laser (Argon-Ion Laser, Krypton-Ion Laser and Mercury-Ion Laser), He-Cd (Helium-Cadmium) Laser, Molecular Gas Laser (CO_2 Laser or Carbon Dioxide Laser), etc.

Semiconductor Lasers: GaAs (Gallium Arsenide) Injection Laser, Doped Semiconductor Laser, C^3 Laser (Cleaved Coupled Cavity Laser), etc.

Chemical Lasers: HCl (Hydrogen Chloride) Laser, HF (Hydrogen Fluoride) Laser, DF-CO_2 Laser, etc.

In this unit we will discuss about Ruby Laser (Solid State Laser), He-Ne Laser (Gas Laser), CO_2 Laser (Molecular Laser) and Nd:YAG Laser (Solid State Laser) in detail.

A solid state Laser is a Laser that uses a gain medium that is a solid, rather than a liquid as in dye Lasers or a gas as in gas Lasers. Semiconductor-based Lasers are also in the solid state, but are generally considered as a separate class from solid state Lasers. Generally, the active medium of a solid state Laser consists of a glass or crystalline 'Host' material, to which is added a 'Dopant', such as Neodymium, Chromium, Erbium, Thulium or Ytterbium. Many of the common dopants are rare-earth elements, because the excited states of such ions are not strongly coupled with the thermal vibrations of their crystal lattices (Photons), and their operational thresholds can be reached at relatively low intensities of Laser pumping.

There are many hundreds of solid state media in which Laser action has been achieved, but relatively few types are in widespread use. Of these, probably the most common is Neodymium-doped Yttrium Aluminium Garnet (Nd: YAG). Neodymium-doped Glass (Nd: Glass) and Ytterbium-doped Glasses or Ceramics are used at very high power levels (terawatts) and high energies (mega Joules), for multiple-beam inertial confinement fusion. The first material used for Lasers was synthetic ruby crystals. Ruby Lasers are still used for a few applications, but they are not common because of their low power efficiencies. At room temperature, ruby Lasers emit only short pulses of light, but at cryogenic temperatures they can be made to emit a continuous train of pulses.

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8.3 RUBY AND Nd-YAG

Ruby Laser is in the family of solid state Lasers. This type of Laser was first designed by Maiman in 1960 and still used on a wide scale with high optical quality.

Ruby, a crystalline form of Al_2O_3 doped with Chromium (Cr). Some Al^{+3} ions of Al_2O_3 are replaced by Cr^{+3} ions. The Laser active material of Ruby Laser (pink color) contains 0.05% of Chromium (Cr). These Cr^{+3} ions perform as active centers in a ruby crystal. The energy levels of Cr^{+3} ion shown in Figure 8.1 in Al_2O_3 crystal. By means of optical pumping the ground state ions of Cr^{+3} raises to two upper levels ($^4F_1$ and $^4F_2$; spectro-scopic notation). These two

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excited states give up energies in proportion to the thermal oscillations of the ruby crystal and fall comparatively fast from these two excited states ($^4F_1$ and $^4F_2$) onto two nearly metastable states denoted by $2\bar{A}$ and $\bar{E}$. The $^4A_2$ level is the ground state of ruby Laser.

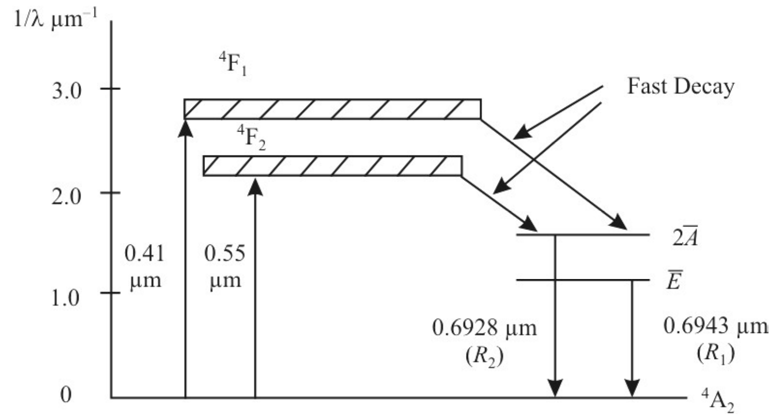


Fig. 8.1 *Energy Levels of Ruby*

The absorption and luminescence spectra of ruby Laser are shown in Figure 8.2 and Figure 8.3. Two absorption spectra of two upper states ($^4F_1$ and $^4F_2$) are of 0.41 μm and 0.55 μm. The emission spectra (luminescence spectra) of the radiation emitted by Cr^{+3} ions consists of 0.6943 μm (R_1-line) and 0.6928 μm (R_2-line).

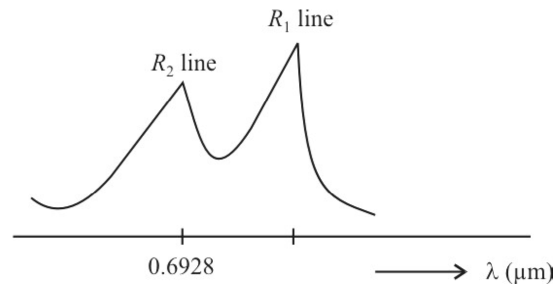


Fig. 8.2 *Luminescence Spectra*

Figure 8.3 shows the schematic diagram of a ruby lasing system.

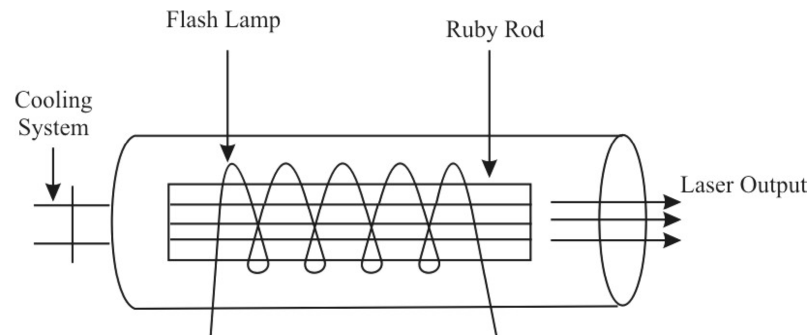


Fig. 8.3 *Ruby Lasing System*

The Nd : YAG Laser

The Neodymium doped Yttrium Aluminium Garnet Laser (Nd: YAG) is in the group of solid state Lasers. It is a four level Laser system having two most intense Lasers of wavelengths 1.0642 m and 1.0615 μm (IR Region). There are atomic energy levels in Neodymium (Nd) ion in Yttrium Aluminium Garnet (YAG) crystal. These five groups of states give rise to five spectral bands in the Nd: YAG absorption spectrum.

The Nd-YAG Laser or Neodymium Yttrium Aluminium Garnet (Nd: YAG (Nd: $Y_3 A_{l5} O_{12}$)) a crystal that is used as a lasing medium for solid state Lasers. It is an optically isotropic crystal in which some of the Y^{3+} ions are replaced by Neodymium Nd^{3+} ions. The dopant, Triply Ionized Neodymium, Nd(III), typically replaces a small fraction (1%) of the Yttrium ions in the host crystal structure of the Yttrium Aluminium Garnet (YAG), since the two ions are of similar size. It is the Neodymium ion which provides the lasing activity in the crystal, in the similar manner as red chromium ion in Ruby Lasers.

The Nd^{3+} acts as active material and the YAG crystal serves as a host.

Source of Energy: Krypton Flash Lamp

Active Medium: Nd: YAG Rod

Optical Cavity: Set of Parallel Mirrors

Construction

The Nd:YAG Laser rod about 10 cm in length and 1 cm in diameter. It is kept in elliptical cylindrical reflector along with a krypton flash lamp. They are placed each at a focus of an elliptical ref lector as shown in Figure 8.4 the light ref lects from the elliptical ref lector and focuses on the Laser rod.

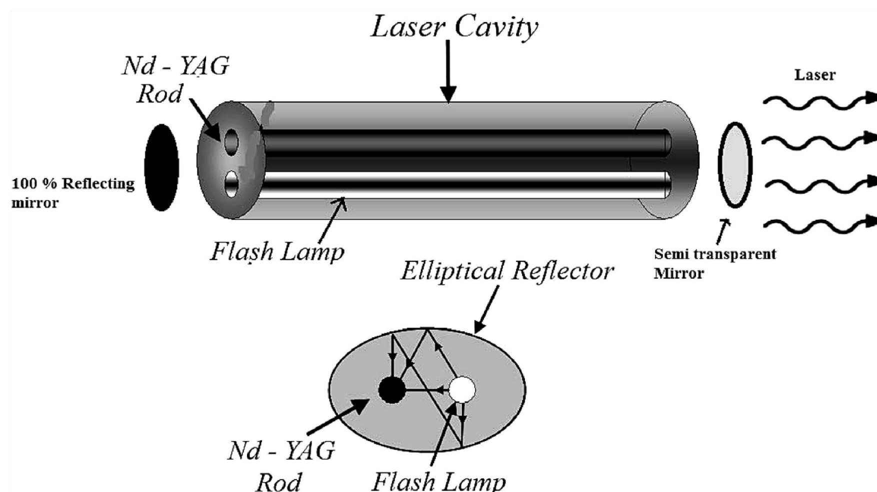


Fig. 8.4 *Nd-YAG Laser*

Working

It is four level pumping schemes. E_4 is upper energy level and E_3 is metastable and upper lasing level. The krypton flash lamp light pumps Nd^{3+} ions to E_4 state. The

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Nd:YAG rod absorbs pump light at a variety of wavelengths in the red and near infrared region of spectrum (7300 Å to 8000 Å). The E_4 level is unstable and Nd^{3+} ions make downward transition rapidly to E_3 level by non -radiative transition. Therefore E_3 level is populated very fast. On the other hand the E_2 level is far above the ground level and cannot be populated through thermal transition from ground state. As population inversion is achieved between E_3 and E_2. Spontaneously emitted photos then stimulate many excited atoms from E_3 to E_2 energy state. The radiation of wavelength 10,600 Å in infrared region is emitted. The Nd^{3+} ions at E_2 level undergo rapid non-radiative transition to the ground level E_1 on their own. Photons generated travel back and forth between two end mirrors. On attaining sufficient strength a Laser beam emerge out through semi-transparent mirror. Nd:YAG Laser

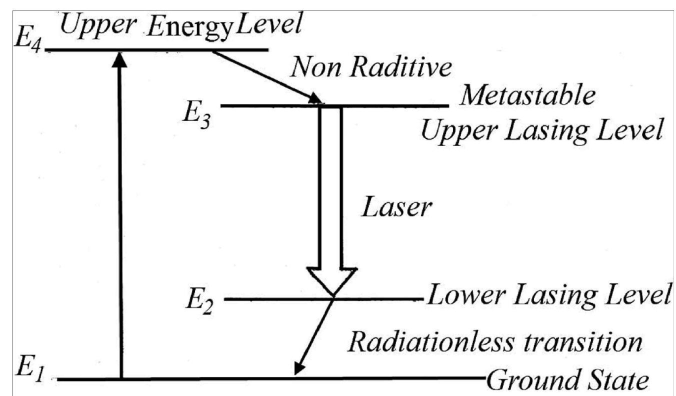


Fig. 8.5 *Energy Level Diagram*

Advantages

Nd-YAG Laser can be operated in continuous as well as pulsed modes.

Drawbacks

Nd-YAG has low efficiency and moderate output. It is the most dangerous Laser for eyes.

Applications

It is extensively used in many industrial applications such as welding of metals and alloys, drilling holes in solid objects, cutting and trimming etc. They are also used in eye surgery, treatment of cancer etc.

8.4 SEMICONDUCTOR LASER

Introduction

Electroluminescence is the basic principle behind the operation of a semiconductor Laser.

NOTES

It is a process in which the electrons from the valence band get excited to conduction band upon applying either DC or AC field. During their deexcitation, the electron and hole recombine to emit light.

Among the semiconductors there are direct band and indirect band semiconductors. In direct band semiconductors the recombination of an electron and a hole takes place directly thereby emitting photons. Hence used for Laser action.

Based on the number of semiconducting materials used in the fabrication of p-n junctions, the semiconductor Lasers are classified as homojunction Lasers and heterojuction Lasers.

Note:

- Semiconductor materials can be classified as direct band gap semiconductors and indirect band gap semiconductors.
  - **(a) Indirect Band Gap Semiconductors:** In the indirect band gap semiconductors like Germanium and Silicon, electrons and holes recombine radiatively, producing no light.
  - **(b) Direct Band Gap Semiconductors:** In the case of direct band gap semiconductors, light gets generated by a direct recombination of an electron and a hole. For this reason, direct band gap materials, such as GaAs are most appropriate and efficient material for generation of light.

There are following two types of radiative recombination.

- In the first radiative recombination process, light emission takes place due to spontaneous emission. The light produced by this process is incoherent, randomly polarised and randomly directed. LEDs (Light Emitting Diodes) emit light by spontaneous emission.
- The second radiative recombination requires the presence of stimulating light wave to trigger the recombination. The light produced by this stimulated process is coherent, highly monochromatic and more directional. Lasers make use of these stimulated emissions to produce their light.

Semiconductor Laser is also called as Laser diode or injection Laser diode. Semiconductor Laser are called so, because the charge carriers are injected across the p-n junction upon applying a DC field.

Check Your Progress

1. Give the definition of solid state Laser.
2. Who invented the Ruby Laser?
3. Write the value of wavelength which has most intense Laser (in IR region).
4. Explain the process of semiconductor Laser.

8.5 Ga As/Al Ga As SEMICONDUCTOR LASER

NOTES

Homojunction

Homojunction is a p-n junction formed with a single semiconductor, such that the basic material has been the same on both sides of the junction. The normal p-n junction is formed in this manner.

Construction

A homojunction GaAs Semiconductor Laser is shown in Figure 8.6. In this type of Laser, the p-n junction is fabricated in a single semiconductor.

The active medium is a p-n junction made from GaAs. The p-region and n-region in the diode are obtained by doping germanium and tellurium, respectively, in GaAs.

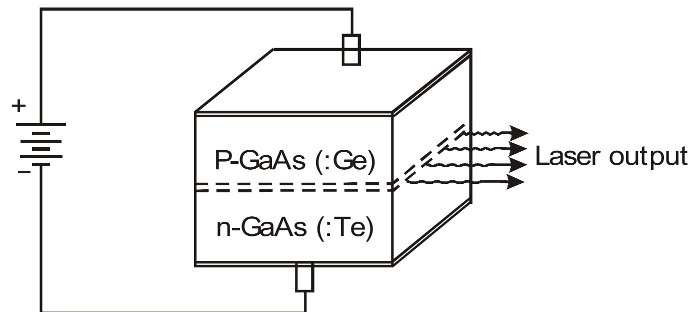


Fig. 8.6 *Homojunction GaAs Semiconductor Laser*

The thickness of the p-n junction layer is made very thin, typically of the order of few microns and the end faces of the crystal are made partially reflecting to form an optical resonator. Electric current is applied to the crystal through metal electrodes fixed on its upper and lower surfaces.

Working

The population inversion is achieved by injecting electrons across the junction from the n-region to the p-regions by means of a forward biasing voltage applied across it.

The recombination of electrons and holes in the region result in the emission of photons. The process is spontaneous and the Laser radiation is random and incoherent. But these photons trigger the stimulated emission of photons to get generated by increasing the rate of recombination of electrons and holes.

In addition to this, if the current density is increased, the emission becomes more and more coherent and the radiation intensity increases. Thus, we get stimulated emission of radiation along the p-n junction, as shown in Figure 8.6.

NOTES

The wavelength of the emitted light radiation depends upon the concentration of donor and acceptor atoms in GaAs and also on the energy gap of the particular semiconductor.

Calculation of Wavelength of Emitted Radiation

Suppose the band gap of GaAs is 1.44 eV, then the band gap is

$$E_g = h\nu = \frac{hc}{\lambda}$$

$$\therefore \quad \lambda = \frac{hc}{E_g} = \frac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{1.44 \times 1.6 \times 10^{-19}} = \mathbf{8626.30\ \text{Å}}$$

Thus, GaAs Laser emits infrared radiation.

Advantages

1. The modulation of the output is possible by controlling the junction current.
2. It is small in dimension but exhibits high efficiency.
3. The fabrication is easy. It can give a continuous wave output.

Disadvantages

1. The output is usually in the form of a wide beam, i.e., it has large beam divergence.
2. Threshold current density is very high.
3. The monochromaticity and coherence are poorer than in other types of Laser.

Applications

1. It is used in long haul communication.
2. It is used in Local Area Networks (LAN) and in CDs.
3. It is used in Laser printers.

Note: Explanation of the operation of a Laser diode based on band theory

- **Absorption:** By absorbing a photon of energy ($E_c - E_v$), an electron in the valence band can make an upward transition to the conduction band.

  $E_v \rightarrow$ Maximum energy of the valence band.

  $E_c \rightarrow$ Minimum energy of the conduction band.
- **Spontaneous Emission:** An electron from the conduction band can recombine with a hole in the valence band and spontaneously emit a photon of energy ($E_c - E_v$).
- **Stimulated Emission:** In the presence of an inducing or stimulating photon, an electron from the conduction can recombine with a hole in the valence band giving stimulated emission. The emitted photon and the inducing photon

travel in the same direction with the same frequency. Thus, the emitted Laser beam is fully coherent.

Heterojunction Semiconductor Laser

Definition 1: A heterojunction is an interface between two adjoining single crystal semiconductors with different band gap energies.

Definition 2: A heterojunction is a junction between two different semiconductor materials.

The heterojunction semiconductor Laser has more additional features and many of the drawbacks of a homojunction semiconductor Laser are overcome.

Principle

The basic working principle of a heterojunction Laser diode is same as that of the homojunction Laser diode.

Construction

A typical double heterojunction GaAs semiconductor Laser diode is shown in Figure 8.7.

In the GaAs diode Laser, on a GaAs substrate a layer of GaAs is sandwiched between two layers of GaAlAs which have a wider band gap and a lower refractive index than GaAs.

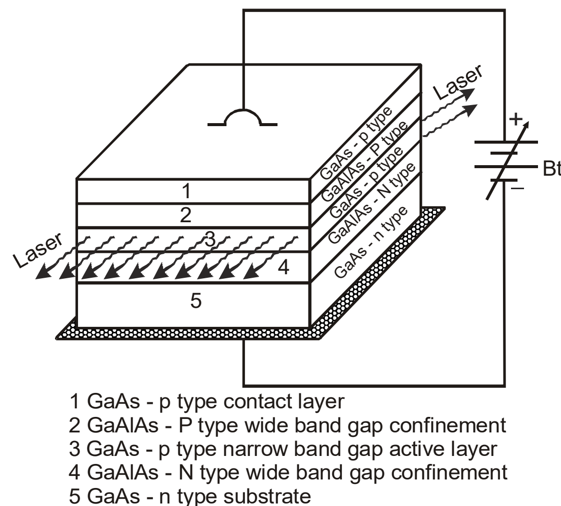


Fig. 8.7 *Double Heterojunction GaAs Semiconductor Laser Diode*

The GaAs diode has N-p-P structure. The N and P layer represent the wider band gap semiconductors GaAlAs and p represent a narrow band gap active layer semiconductor GaAs. A contact layer made of GaAs is formed at the top of GaAlAs - P type. All these four layers are grown over the GaAs substrate.

An external power supply is connected to the heterojunction diode through the electrodes attached to it one at the top and the other at the bottom.

NOTES

Working

When the diode is forward biased with the help of a power supply, the charge injection takes place into the active layer resulting in spontaneous emission of photons. Due to the continuous supply of forward bias voltage a large number of injected charges are available for stimulated recombination and they create population inversion. The stripe geometry provides the confinement of charges in the lateral direction and the longer life for the Laser diodes.

The band gap difference prevents the diffusion of injected charge carriers from the active layer, thus resulting in stimulated emission of radiation which is a coherent Laser radiation. As the front and back faces of the active layer are dielectric coated, they provide sufficient feedback for Laser oscillation.

Thus, a more intense, more coherent, high efficiency and a high power Laser in IR region is produced. The output wavelength is 0.8 μm when the band gap of active layer is 1.55eV.

Advantages

1. Very narrow beam with high coherence and monochromaticity is possible.
2. Continuous wave output is possible.
3. Threshold current density is very low.
4. It is more stable and has longer life time.
5. Carrier confinement and optical confinement can be achieved simultaneously.

Disadvantages

1. Cost is higher than homojunction Laser.
2. p-n junction crystal growth is more difficult.

Distinguish Homojunction and Heterojunction Laser Diodes

S.No.	*Homojunction laser diode*	*Heterojunction laser diode*
1.	The junction is made of single crystal of same type.	The junction is made of two different semiconductor materials.
2.	Pulsed output.	Continuous output.
3.	Power output is low.	Power output is high.
4.	Life time is less.	Life time is more.
5.	Low cost.	High cost.

Example 8.1

For InP Laser diode, the wavelength of light emission is 1.55 μm. What is its band gap in eV?

Solution:

Given, $\lambda = 1.55$; $\mu m = 1.55 \times 10^{-6}$ m; $E_g = ?$

Formula: $E_g = \dfrac{hc}{\lambda} = \dfrac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{1.55 \times 10^{-6} \times 1.6 \times 10^{-19}} = \dfrac{1.9875 \times 10^{-25}}{2.48 \times 10^{-25}}$

$\therefore$ $\mathbf{E_g = 0.8014\ eV.}$

NOTES

Example 8.2

Calculate the long wavelength limit of an extrinsic semiconductor if the ionisation energy is 0.02 eV.

Solution:

Given, $E = 0.02\ \text{eV} = 0.02 \times 1.6 \times 10^{-19}$ J

Formula: $\lambda = \dfrac{hc}{E} = \dfrac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{0.02 \times 1.6 \times 10^{-19}} = \dfrac{1.9875 \times 10^{-25}}{3.2 \times 10^{-21}}$

$\therefore$ $\mathbf{\lambda = 6.2109 \times 10^{-5}\ m.}$

Example 8.3

A Laser source emits light of wavelength 0.621 μm and has an output of 35 mW. Calculate how many photons are emitted per minute by this Laser source.

Solution:

Given, the power output, i.e., the total energy

$$E = 3.5\ \text{mW}$$

$$= 3.5 \times 10^{-3}\ \text{Js}^{-1} = 3.5 \times 10^{-3} \times 60\ \text{J/minute}$$

$$\lambda = 0.621\ \mu\text{m} = 0.621 \times 10^{-6}\ \text{m}$$

The frequency of the photon emitted is given by

$$\nu = \frac{c}{\lambda}$$

$$\therefore \quad \nu = \frac{3 \times 10^{8}}{0.621 \times 10^{-6}}$$

$$\mathbf{\nu = 4.8309 \times 10^{14}\ Hz}$$

But we know, $E = h\nu$

$$\therefore \quad E = 6.625 \times 10^{-34} \times 4.8309 \times 10^{14}$$

$$\mathbf{E = 3.200 \times 10^{-19}\ J.}$$

This is the energy emitted by one photon.

Therefore, the number of photons emitted per minute is

$$n = \frac{\text{total energy emitted per minute}}{\text{energy of one photon}}$$

$$\therefore \quad n = \frac{3.5 \times 10^{-3} \times 60}{3.200 \times 10^{-19}} = \frac{0.21}{3.2 \times 10^{-19}}$$

$$\mathbf{n = 6.562 \times 10^{17}\ photons/minute.}$$

NOTES

Example 8.4

Laser action occurs by the transition from an excited state (E_2) to the ground state ($E_1 = 0$). If the transition produces a light of wavelength 6,930 Å, find the energy level of the excited state.

Solution:

Given, $\lambda = 6.930\times10^{-7}$ m, $h = 6.626\times10^{-34}$ Js, $c = 3\times10^8$ ms^{-1} and $E_1 = 0$.

We know, $$E_2 - E_1 = h\nu = \frac{hc}{\lambda}.$$

Substituting the given values in above equation we have

$$E_2 - E_1 = E_2 = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^8}{6.93\times10^{-7}}.$$

So, the energy level of the excited state is

$$\mathbf{E_2 = 2.8683\times10^{-19}\ J = 1.7927\ eV}.$$

Example 8.5

An atom is stimulated from the state of energy of 1×10^{-34} J to an excited level of 7.62×10^{-34} J. What is the frequency of the stimulating photon?

Solution:

Given, Energy of an atom in ground state $E_1 = 1 \times 10^{-34}$ J

Energy of an atom in excited state $E_2 = 7.62 \times 10^{-34}$ J

Planck's constant $h = 6.625 \times 10^{-34}$ J-s

We know that $E_2 - E_1 = h\nu$

$$\therefore \qquad \nu = \frac{E_2 - E_1}{h}$$

Substituting values in above equation

$$\nu = \frac{7.62\times10^{-34} - 1.0\times10^{-34}}{6.625\times10^{-34}}$$

Hence the frequency of the stimulating photon is $\nu =$ **1.0 Hz.**

Example 8.6

In a Laser action the energy of the stimulating photon is 39.62×10^{-20} J. What is the wavelength of the stimulating photon?

Solution:

Given, Energy of the stimulating photon $E = 39.62 \times 10^{-35}$ J

Planck's constant '*h*' $= 6.625 \times 10^{-34}$ J-s

NOTES

We know that $E = h\nu$

$$\therefore \qquad \nu = \frac{E}{h}$$

Substituting values in above equation

$$\nu = \frac{39.62 \times 10^{-20}}{6.625 \times 10^{-34}} = 5.98 \times 10^{14} \text{ Hz}$$

We know that $c = \nu\lambda$

$$\therefore \qquad \lambda = \frac{c}{\nu} = \frac{3 \times 10^{8}}{5.98 \times 10^{14}} = 5.0167 \times 10^{-7}$$

Thus, the wavelength of the stimulating photon is $\boldsymbol{\lambda = 5.0167 \times 10^{-7}}$ **m**.

8.6 GAS LASER

Laser cutting is a technology that uses a Laser to cut materials. The most popular Lasers for cutting materials are CO_2 and Nd : YAG.

Process

Laser cutting of metals is generally done with the help of gas, like air, oxygen, nitrogen or argon which is directed into the cut through a nozzle.

When a high power Laser beam is focussed at the surface of the material to be cut it melts the material. The melted material can be removed by making use of a gas jet coaxial with the Laser as shown in Figure 8.8.

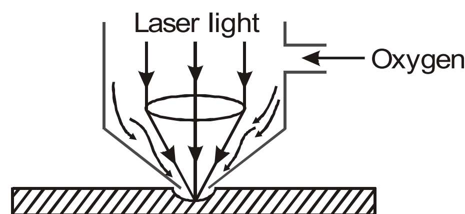


Fig. 8.8 *Laser Cutting*

The Laser focussing part is surrounded by a nozzle into which oxygen gas is passed. When Laser heats up the material, it interacts with the gas and the gas gets combustion. The combustion of the gas burns the metal thus reducing the Laser power requirement for cutting.

The tiny splinters along with the molten part of the metal will be blown away by the oxygen jet. The gas jet also help in removing the molten material. It is the Laser and not the burning gas which controls the accuracy of cutting. Thus, the cut edges will be of very high quality.

NOTES

Oxygen is used in cases where oxidation of the edge is allowable. The cutting rate gets increased when oxygen is used for cutting metals due to the reaction between the oxygen and molten metal.

To cut materials that are oxide free, like wood, paper, plastic, etc., instead of oxygen inert gases like nitrogen or argon is used.

Applications of Laser in Cutting

1. Laser cutting is used to cut all types of metals including carbon, stainless and zinc coated steel, super alloys, aluminium, titanium etc.
2. Laser cutting is also used for cutting plastics and ceramics.
3. Laser cutting can also be used to cut materials coated with enamel, porcelain or ceramics without causing any damage to the outer coating.
4. Laser are also used in garment industry to cut dozens to hundreds of thickness of cloth.
5. Laser cutting of stainless steel nickel alloys and other metals find widespread application in the aircraft and automobile industries.

Advantages of Laser Cutting

The advantages of Laser cutting are,

1. *Flexibility* - The range of materials to which Laser cutting can be applied.
2. *Edge quality* - The Laser cutting results in high quality edges which can be painted without additional finishing.
3. *Easy automation* - Can easily automated to limited operator involvement and even 'Light Out' operation.
4. *Distortion free* - There is no physical contact between the workpiece and the cutting tool.
5. High precision.

8.7 He-Ne AND CO_2 LASERS

The He-Ne Laser was the first gas Laser to be operated successfully; fabricated by Ali Javan and his co-workers in Bell Telephone Laboratory in USA in 1961.

In this Laser mixture of Helium (He) and Neon (Ne) is used as the Laser active medium. Here He atoms plays an improtant role for the excitation of the Ne atoms. The He-Ne Laser is excited by a stationary glow discharged by DC current. Eventually, Laser active metastable states are not present in He. The 3*s* and 2*s* bands are the two metastable states of Ne. Energy states $1s_0$ and $2s_1$ of He are very close in height to the 3*S* and 2*S* states of Ne. Difference between them is about 200 cm^{-1} only.

NOTES

He-Ne Laser action occurs on the three possible transitions — 3*s* to 3*p*, 3*s* to 2*p* and 2*s* to 2*p*; out of which the radiation from 3*s* to 2*p* is in visible region (red) of wavelength 0.6328 μm. Other two radiations (3.39 μm and 1.15 μm) are in infra-red region. Energy level diagram of He-Ne Laser is shown in Figure 8.9 and Figure 8.10.

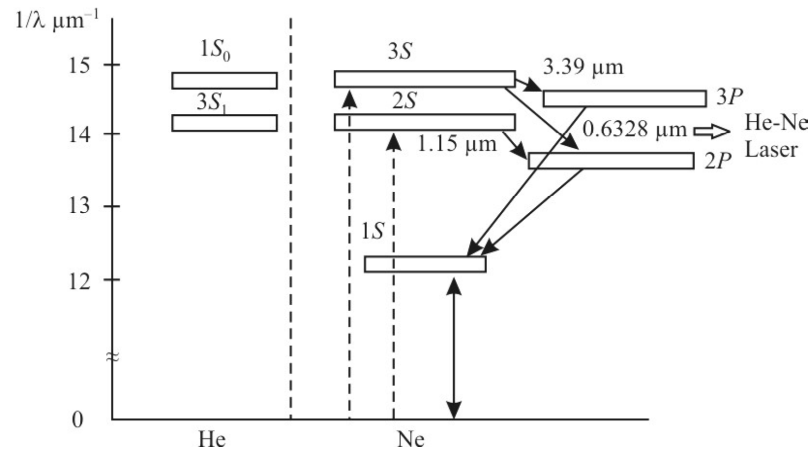


Fig. 8.9 *Energy Level Diagram of He-Ne Laser*

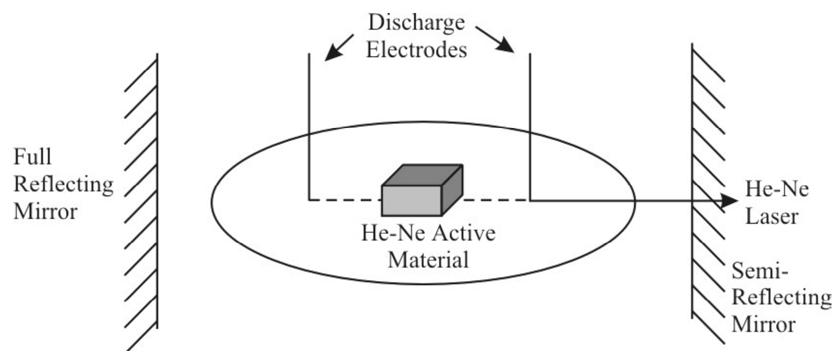


Fig. 8.10 *He-Ne Lasing System*

The CO_2 Laser

It is in the group of molecular Lasers and invented by C.K.M. Patel. In CO_2, state 2 and 5 are the metastable states. The configuration of CO_2 is O–C–O, having no permanent dipole moment.

The life time of vibrational state 1 is much lower than that of rotational state 2. Thus, we consider only rotational state 2 for lasing action. The schematic diagram of CO_2 Laser has been shown in Figure 8.11. When an electrical energy incident on the Laser active material, the molecular property broken. In this Laser CO_2 and N_2 molecules mixture are used as Laser active material. The N_2 molecules take the role as He plays in He-Ne Laser. At first, we get pulsed Laser, as there are two metastable states in CO_2 and when the radiations lastly come down to stable state, we get continuous Laser. There are two transitions of wavelengths 10.6 and 9.6 mm (IR region).

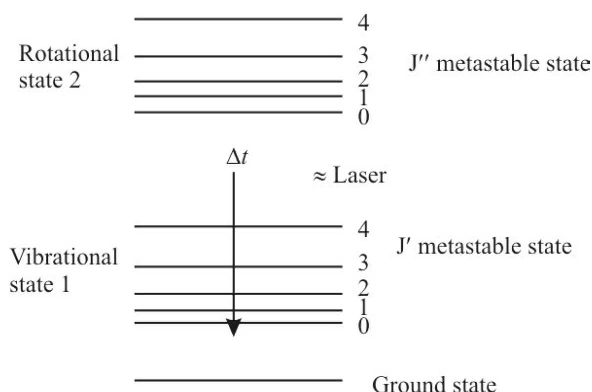


Fig. 8.11 *Schematic Diagram of CO_2 Laser*

Check Your Progress

5. What is homojunction?
6. Write the advantage of Laser cutting.
7. Explain the energy state of He-Ne Laser.

8.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Solid state Lasers: In this category, there are different types of Laser system, for example Ruby Laser, Nd: YAG Laser, U^{+3} in CaF_2 Laser, etc.
2. This type of Laser was first designed by Maiman in 1960 and still used on a wide scale with high optical quality.
3. The neodymium doped yttrium aluminium garnet Laser is in the group of solid state Lasers. It is a four level Laser system having two most intense Lasers of wavelengths 1.0642 mm and 1.0615 mm (IR region).
4. Electroluminescence is the basic principle behind the operation of a semiconductor Laser.

   It is a process in which the electrons from the valence band get excited to conduction band upon applying either DC or AC field. During their deexcitation, the electron and hole recombine to emit light.
5. Homojunction is a p-n junction formed with a single semiconductor, such that the basic material has been the same on both sides of the junction. The normal p-n junction is formed in this manner.
6. The advantages of Laser cutting are,
   (i) Flexibility - The range of materials to which Laser cutting can be applied.
   (ii) Edge quality - The Laser cutting results in high quality edges which can be painted without additional finishing.

NOTES

(iii) Easy automation - Can easily automated to limited operator involvement and even 'Light Out' operation.

(iv) Distortion free - There is no physical contact between the workpiece and the cutting tool.

(v) High precision.

8. Energy state of He-Ne Laser $1s_0$ and $2s_1$ of He are very close in height to the $3S$ and $2S$ states of Ne. Difference between them is about 200 cm^{-1} only.

8.9 SUMMARY

- Solid state Lasers: In this category, there are different types of Laser system *e.g.* ruby Laser, Nd: YAG Laser, U^{+3} in CaF_2 Laser etc.
- Ruby Laser is in the family of solid state Lasers. This type of Laser was first designed by Maiman in 1960 and still used on a wide scale with high optical quality.
- Optical pumping the ground state ions of Cr^{+3} raises to two upper levels ($^4F_1$ and $^4F_2$; spectro-scopic notation). These two excited states give up energies in proportion to the thermal oscillations of the ruby crystal and fall comparatively fast from these two excited states ($^4F_1$ and $^4F_2$) onto two nearly metastable states denoted by $2\overline{A}$ and $\overline{E}$. The $^4A_2$ level is the ground state of ruby Laser.
- Two absorption spectra of two upper states ($^4F_1$ and $^4F_2$) are of 0.41 μm and 0.55 μm. The emission spectra (luminescence spectra) of the radiation emitted by Cr^{+3} ions consists of 0.6943 mm (R_1-line) and 0.6928 mm (R_2-line).
- The neodymium doped yttrium aluminium garnet Laser is in the group of solid state Lasers. It is a four level Laser system having two most intense Lasers of wavelengths 1.0642 mm and 1.0615 mm (IR region).
- Electroluminescence is the basic principle behind the operation of a semiconductor Laser.
- It is a process in which the electrons from the valence band get excited to conduction band upon applying either d.c. or AC field. During their deexcitation, the electron and hole recombine to emit light.
- Semiconductor materials can be classified as direct band gap semi conductors and indirect band gap semiconuctors.
- In the first radiative recombination process, light emission takes place due to spontaneous emission. The light produced by this process is incoherent, randomly polarised and randomly directed. LEDs emit light by spontaneous emission.

NOTES

- The second radiative recombination requires the presence of stimulating light wave to trigger the recombination. The light produced by this stimulated process is coherent, highly monochromatic and more directional. Lasers make use of these stimulated emissions to produce their light.
- Semiconductor Laser is also called as Laser diode or injection Laser diode. Semiconductor Laser are called so, because the charge carriers are injected across the pn junction upon applying a d.c. field.
- Homojunction is a p-n junction formed with a single semiconductor, such that the basic material has been the same on both sides of the junction. The normal pn junction is formed in this manner.
- The population inversion is achieved by injecting electrons across the junction from the n-region to the p-regions by means of a forward biasing voltage applied across it.
- The basic working principle of a heterojunction Laser diode is same as that of the homojunction Laser diode.
- In the GaAs diode Laser, on a GaAs substrate a layer of GaAs is sandwiched between two layers of GaAlAs which have a wider band gap and a lower refractive index than GaAs.
- Laser cutting is a technology that uses a Laser to cut materials. The most popular Lasers for cutting materials are CO_2 and Nd : YAG.
- When a high power Laser beam is focussed at the surface of the material to be cut it melts the material. The melted material can be removed by making use of a gas jet coaxial with the Laser.
- Oxygen is used in cases where oxidation of the edge is allowable. The cutting rate gets increased when oxygen is used for cutting metals due to the reaction between the oxygen and molten metal.
- He-Ne Laser action occurs on the three possible transitions — 3*s* to 3*p*, 3*s* to 2*p* and 2*s* to 2*p*; out of which the radiation from 3*s* to 2*p* is in visible region (red) of wavelength 0.6328 μm. Other two radiations (3.39 μm and 1.15 μm) are in infra-red region.
- The N_2 molecules take the role as He plays in He-Ne Laser. At first, we get pulsed Laser, as there are two metastable states in CO_2 and when the radiations lastly come down to stable state, we get continuous Laser. There are two transitions of wavelengths 10.6 and 9.6 mm (IR region).

8.10 KEY WORDS

- **Solid State Lasers:** A solid state Laser is a Laser that uses a gain medium that is a solid, rather than a liquid as in dye Lasers or a gas as in gas Lasers. In this category, there are different types of Laser systems, for example Ruby Laser, Nd: YAG Laser, U^{+3} in CaF_2 Laser, etc.

NOTES

- **Gas Lasers:** He-Ne (Helium-Neon) Laser, Ion Laser (Argon-Ion Laser, Krypton-Ion Laser and Mercury-Ion Laser), He-Cd (Helium-Cadmium) Laser, Molecular Gas Laser (CO_2 Laser or Carbon Dioxide Laser), etc.
- **Semiconductor Lasers:** GaAs (Gallium Arsenide) Injection Laser, Doped Semiconductor Laser, C^3 Laser (Cleaved Coupled Cavity Laser), etc.
- **Chemical Lasers:** HCl (Hydrogen Chloride) Laser, HF (Hydrogen Fluoride) Laser, DF-CO_2 Laser, etc.
- **Indirect band gap semiconductors:** In the indirect band gap semiconductors like Germanium and Silicon, electrons and holes recombine radiatively, producing no light.
- **Direct band gap semiconductors:** In the case of direct band gap semiconductors, light gets generated by a direct recombination of an electron and a hole. For this reason, direct band gap materials, such as GaAs are most appropriate and efficient material for generation of light.
- **Spontaneous emission:** An electron from the conduction band can recombine with a hole in the valence band and spontaneously emit a photon of energy ($E_c – E_v$).
- **Stimulated emission:** In the presence of an inducing or stimulating photon, an electron from the conduction can recombine with a hole in the valence band giving stimulated emission. The emitted photon and the inducing photon travel in the same direction with the same frequency. Thus, the emitted Laser beam is fully coherent.

8.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Explain about the solid state Laser and its uses.
2. Define the term of Ruby and Nd-YAG Laser.
3. Give the classification of semiconductor material.
4. Give the advantage and disadvantage of GaAs semiconductor Laser.
5. Explain the application of gas Laser.
6. What is He-Ne Laser?
7. Explain about the CO_2 Laser.

Long-Answer Questions

1. Explain the solid state Laser giving its uses and types.
2. Elaborate on the working mechanism of Ruby Laser with schematic diagram.

3. Discuss about the construction, working advantages, drawback and applications of Nd-YAG laser.
4. Briefly discuss about the characteristic features and the introduction and classification of semiconductor Laser.
5. Elaborate on the GaAs semiconductor Laser giving its applications.
6. Briefly explain about the gas Laser and its application.
7. Explain about the energy level diagram of He-Ne and CO_2 Laser.

NOTES

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UNIT 9 NON-LINEAR OPTICAL PROPERTIES OF MATERIALS

Structure

9.0 INTRODUCTION

NonLinear Optics (NLO) is the branch of optics that describes the behaviour of light in nonlinear media, that is, media in which the polarisation density 'P' responds non-linearly to the electric field 'E' of the light. The non-linearity is typically observed only at very high light intensities (values of atomic electric fields, typically 10^8 V/m), such as those provided by Lasers. Above the Schwinger limit, the vacuum itself is expected to become nonlinear. In nonlinear optics, the superposition principle no longer holds.

The first nonlinear optical effect to be predicted was two-photon absorption, by Maria Goeppert Mayer for her PhD in 1931, but it remained an unexplored theoretical curiosity until 1961 and the almost simultaneous observation of two-photon absorption at Bell Labs and the discovery of second-harmonic generation by Peter Franken et al. at University of Michigan, both shortly after the construction of the first Laser by Theodore Maiman. However, some nonlinear effects were discovered before the development of the Laser. The theoretical basis for many nonlinear processes were first described in Bloembergen's monograph 'Nonlinear Optics'

Nonlinear effects fall into two qualitatively different categories, parametric and non-parametric effects. A parametric non-linearity is an interaction in which the quantum state of the nonlinear material is not changed by the interaction with

the optical field. As a consequence of this, the process is 'Instantaneous'. Energy and momentum are conserved in the optical field, making phase matching important and polarisation-dependent.

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The early studies of nonlinear optics and materials focused on the inorganic solids. With the development of nonlinear optics, molecular optical properties were investigated, forming molecular nonlinear optics. The traditional approaches used in the past for enhancing nonlinearities include extending chromophore π-systems, adjusting bond length alternation, inducing intramolecular charge transfer, extending conjugation in 2D (Two Dimensional), and engineering multipolar charge distributions. Recently, many novel directions were proposed for enhanced nonlinearity and light manipulation, including twisted chromophores, combining rich density of states with bond alternation, microscopic cascading of second-order nonlinearity, etc. Due to the distinguished advantages, molecular nonlinear optics have been widely used in the bio photonics field, including bio imaging, phototherapy, bio sensing, etc.

In this unit, you will study about the Electro-Optic effect, Pockel's effect, Kerr effect, second harmonic generators, Electro-Optic modulators, photorefractive materials, acousto-optic effect.

9.1 OBJECTIVES

After going through this unit, you will be able to:

- Define the electro-optic effect
- Understand the significance of Pockel's effect
- Explain about the Kerr effect
- Analyse the second harmonic generators
- Discuss the electro-optic modulators
- Understand the photorefractive materials
- Define the acousto-optic effect

9.2 ELECTRO-OPTIC EFFECT

An electro-optic effect is a change in the optical properties of a material in response to an electric field that varies slowly compared with the frequency of light. The term encompasses a number of distinct phenomena, which can be subdivided into some important segments as change of the absorption and change of the refractive index and permittivity. The change of absorption deals with the Electro absorption: general change of the absorption constants, Franz-Keldysh effect, Quantum-confined Stark effect, and Electrochromic effect, etc. While change of the refractive index and permittivity involves the Pockels effect, Kerr effect, electro-gyration effect, and Electron-refractive effect.

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Changes in absorption can have a strong effect on refractive index for wavelengths near the absorption edge, due to the Kramers–Kronig relation. Using a less strict definition of the electro-optic effect allowing also electric fields oscillating at optical frequencies, one could also include nonlinear absorption (absorption depends on the light intensity) to category a) and the optical Kerr effect (refractive index depends on the light intensity) to category b). Combined with the photoeffect and photoconductivity, the electro-optic effect gives rise to the photorefractive effect. The term "Electro-Optic" is often erroneously used as a synonym for "Optoelectronic".

9.3 POCKEL'S EFFECT

The Pockel's effect (after Friedrich Carl Alwin Pockels who studied the effect in 1893), or Pockel's electro-optic effect, changes or produces birefringence in an optical medium induced by an electric field. In the Pockel's effect, also known as the linear electro-optic effect, the birefringence is proportional to the electric field. In the Kerr effect, the refractive index change (birefringence) is proportional to the square of the field. The Pockel's effect occurs only in crystals that lack inversion symmetry, such as lithium niobate, and in other noncentrosymmetric media such as electric-field poled polymers or glasses.

9.4 KERR EFFECT

The Kerr effect, also called the Quadratic Electro-Optic (QEO) effect, is a change in the refractive index of a material in response to an applied electric field. The Kerr effect is distinct from the Pockel's effect in that the induced index change is directly proportional to the square of the electric field instead of varying linearly with it. All materials show a Kerr effect, but certain liquids display it more strongly than others. The Kerr effect was discovered in 1875 by John Kerr, a Scottish physicist. Two special cases of the Kerr effect are normally considered, these being the Kerr electro-optic effect, or DC Kerr effect, and the optical Kerr effect, or AC Kerr effect.

The Kerr electro-optic effect, or DC Kerr effect, is the special case in which a slowly varying external electric field is applied by, for instance, a voltage on electrodes across the sample material. Under this influence, the sample becomes birefringent, with different indices of refraction for light polarised parallel to or perpendicular to the applied field. The difference in index of refraction, Än, is given by

$$\Delta n = \lambda K E^2,$$

Where λ is the wavelength of the light, K is the Kerr constant, and E is the strength of the electric field. This difference in index of refraction causes the material to act like a wave plate when light is incident on it in a direction perpendicular to

the electric field. If the material is placed between two 'Crossed' (perpendicular) linear polarizers, no light will be transmitted when the electric field is turned off, while nearly all of the light will be transmitted for some optimum value of the electric field. Higher values of the Kerr constant allow complete transmission to be achieved with a smaller applied electric field.

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Check Your Progress

1. Explain the term electro-optic effect.
2. Write the state of Pockel's effect.
3. Elaborate on the Kerr effect.
4. Write the equation of index of refraction in Kerr effect.

9.5 SECOND HARMONIC GENERATORS

Second-Harmonic Generation (SHG, also called frequency doubling) is a nonlinear optical process in which two photons with the same frequency interact with a nonlinear material, are 'Combined', and generate a new photon with twice the energy of the initial photons (equivalently, twice the frequency and half the wavelength), that conserves the coherence of the excitation. It is a special case of sum-frequency generation (2 photons), and more generally of harmonic generation.

The second-order non-linear susceptibility of a medium characterizes its tendency to cause SHG. Second-harmonic generation, like other even-order nonlinear optical phenomena, is not allowed in media with inversion symmetry (in the leading electric dipole contribution). However, effects such as the Bloch–Siegert shift (oscillation), found when two-level systems are driven at Rabi frequencies comparable to their transition frequencies, will give rise to second harmonic generation in Centro-symmetric systems. In addition, in non-centrosymmetric crystals belonging to crystallographic point group 432, the SHG is not possible and under Kleinman's conditions SHG in 422 and 622 point groups should vanishes although some exceptions exist.

Generating the second harmonic, often called frequency doubling, is also a process in radio communication; it was developed early in the 20th century, and has been used with frequencies in the megahertz range. It is a special case of frequency multiplication.

9.6 ELECTRO-OPTIC MODULATORS

An Electro-Optic Modulator (EOM) is an optical device in which a signal-controlled element exhibiting an electro-optic effect is used to modulate a beam of light. The modulation may be imposed on the phase, frequency, amplitude, or

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polarisation of the beam. Modulation bandwidths extending into the gigahertz range are possible with the use of laser-controlled modulators.

The simplest kind of EOM consists of a crystal, such as lithium niobate, whose refractive index is a function of the strength of the local electric field. That means that if lithium niobate is exposed to an electric field, light will travel more slowly through it. But the phase of the light leaving the crystal is directly proportional to the length of time it takes that light to pass through it. Therefore, the phase of the laser light exiting an EOM can be controlled by changing the electric field in the crystal.

Liquid crystal devices are electro-optical phase modulators if no polarizers are used.

9.7 PHOTOREFRACTIVE MATERIALS

A photorefractive material is illuminated by coherent beams of light. (In holography, these would be the signal and reference beams). Interference between the beams results in a pattern of dark and light fringes throughout the crystal.

The photorefractive effect can be used for dynamic holography, and, in particular, for cleaning of coherent beams. For example, in the case of a hologram, illuminating the grating with just the reference beam causes the reconstruction of the original signal beam. When two coherent laser beams (usually obtained by splitting a laser beam by the use of a beamsplitter into two, and then suitably redirecting by mirrors) cross inside a photorefractive crystal, the resultant refractive index grating diffracts the laser beams. As a result, one beam gains energy and becomes more intense at the expense of light intensity reduction of the other. This phenomenon is an example of two-wave mixing. In this configuration, Bragg diffraction condition is automatically satisfied.

9.8 ACOUSTO-OPTIC EFFECT

Acousto-optics is a branch of physics that studies the interactions between sound waves and light waves, especially the diffraction of laser light by ultrasound (or sound in general) through an ultrasonic grating. In general, acousto-optic effects are based on the change of the refractive index of a medium due to the presence of sound waves in that medium. Sound waves produce a refractive index grating in the material, and it is this grating that is 'Seen' by the light wave. These variations in the refractive index, due to the pressure fluctuations, may be detected optically by refraction, diffraction, and interference effects, reflection may also be used.

The acousto-optic effect is extensively used in the measurement and study of ultrasonic waves. However, the growing principal area of interest is in acousto-optical devices for the deflection, modulation, signal processing and frequency shifting of light beams. This is due to the increasing availability and performance of

lasers, which have made the acousto-optic effect easier to observe and measure. Technical progress in both crystal growth and high frequency piezoelectric transducers has brought valuable benefits to acousto-optic components' improvements.

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Check Your Progress

5. What is Second-Harmonic Generator (SHG)?
6. What do you understand by electro-optic modulators?
7. Elaborate on the photorefractive materials.
8. Define the features of acousto-optics effect.

9.9 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. An electro-optic effect is a change in the optical properties of a material in response to an electric field that varies slowly compared with the frequency of light. The term encompasses a number of distinct phenomena, which can be subdivided into some important segments as change of the absorption and change of the refractive index and permittivity.
2. Pockel's effect, also known as the linear electro-optic effect, the birefringence is proportional to the electric field.
3. The Kerr effect, also called the Quadratic Electro-Optic (QEO) effect, is a change in the refractive index of a material in response to an applied electric field.
4. The difference in index of refraction, An, is given by

   $\Delta n = \lambda K E^2$

   Where the λ wavelength of the light, K is is the Kerr constant, and E is the strength of the electric field.
5. Second-Harmonic Generator (SHG, also called frequency doubling) is a nonlinear optical process in which two photons with the same frequency interact with a nonlinear material, are 'Combined', and generate a new photon with twice the energy of the initial photons (equivalently, twice the frequency and half the wavelength), that conserves the coherence of the excitation.
6. An Electro-Optic Modulator (EOM) is an optical device in which a signal controlled element exhibiting an electro-optic effect is used to modulate a beam of light. The modulation may be imposed on the phase, frequency, amplitude, or polarisation of the beam. Modulation bandwidths extending into the gigahertz range are possible with the use of Laser-controlled modulators.

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7. A photorefractive material is illuminated by coherent beams of light. In holography, these would be the signal and reference beams. Interference between the beams results in a pattern of dark and light fringes throughout the crystal.
8. Acousto-optic effects are based on the change of the refractive index of a medium due to the presence of sound waves in that medium. Sound waves produce a refractive index grating in the material, and it is this grating that is 'Seen' by the light wave. These variations in the refractive index, due to the pressure fluctuations, may be detected optically by refraction, diffraction, and interference effects, reflection may also be used.

9.10 SUMMARY

- An electro-optic effect is a change in the optical properties of a material in response to an electric field that varies slowly compared with the frequency of light. The term encompasses a number of distinct phenomena, which can be subdivided into some important segments as change of the absorption and change of the refractive index and permittivity.
- While change of the refractive index and permittivity involves the Pockels effect, Kerr effect, electro-gyration effect, and Electron-refractive effect.
- Changes in absorption can have a strong effect on refractive index for wavelengths near the absorption edge, due to the Kramers–Kronig relation.
- The Pockel's effect (after Friedrich Carl Alwin Pockels who studied the effect in1893), or Pockel's electro-optic effect, changes or produces birefringence in an optical medium induced by an electric field.
- Pockel's effect, also known as the linear electro-optic effect, the birefringence is proportional to the electric field.
- The Kerr effect is distinct from the Pockel's effect in that the induced index change is directly proportional to the square of the electric field instead of varying linearly with it.
- The Kerr effect was discovered in 1875 by John Kerr, a Scottish physicist. Two special cases of the Kerr effect are normally considered, these being the Kerr electro-optic effect, or DC Kerr effect, and the optical Kerr effect, or AC Kerr effect.
- The Kerr electro-optic effect, or DC Kerr effect, is the special case in which a slowly varying external electric field is applied by, for instance, a voltage on electrodes across the sample material.
- Second-Harmonic Generator (SHG, also called frequency doubling) is a nonlinear optical process in which two photons with the same frequency interact with a nonlinear material, are 'Combined', and generate a new photon with twice the energy of the initial photons (equivalently, twice the

frequency and half the wavelength), that conserves the coherence of the excitation.

- The second-order non-linear susceptibility of a medium characterizes its tendency to cause SHG (Second-Harmonic Generation). Second-harmonic generation, like other even-order nonlinear optical phenomena, is not allowed in media with inversion symmetry (in the leading electric dipole contribution).
- Generating the second harmonic, often called frequency doubling, is also a process in radio communication; it was developed early in the 20th century, and has been used with frequencies in the megahertz range. It is a special case of frequency multiplication.
- An Electro-Optic Modulator (EOM) is an optical device in which a signal controlled element exhibiting an electro-optic effect is used to modulate a beam of light. The modulation may be imposed on the phase, frequency, amplitude, or polarisation of the beam. Modulation bandwidths extending into the gigahertz range are possible with the use of Laser-controlled modulators.
- A photorefractive material is illuminated by coherent beams of light. (In holography, these would be the signal and reference beams). Interference between the beams results in a pattern of dark and light fringes throughout the crystal.
- The photorefractive effect can be used for dynamic holography, and, in particular, for cleaning of coherent beams.
- When two coherent laser beams (usually obtained by splitting a Laser beam by the use of a beam splitter into two, and then suitably
- Splitting a Laser beam by the use of a beam splitter into two, and then suitably redirecting by mirrors) cross inside a photorefractive crystal, the resultant refractive index grating diffracts the Laser beams.
- Acousto-optics is a branch of physics that studies the interactions between sound waves and light waves, especially the diffraction of Laser light by ultrasound (or sound in general) through an ultrasonic grating.
- Acousto-optic effects are based on the change of the refractive index of a medium due to the presence of sound waves in that medium. Sound waves produce a refractive index grating in the material, and it is this grating that is 'Seen' by the light wave. These variations in the refractive index, due to the pressure fluctuations, may be detected optically by refraction, diffraction, and interference effects, reflection may also be used.
- The acousto-optic effect is extensively used in the measurement and study of ultrasonic waves. However, the growing principal area of interest is in acousto-optical devices for the deflection, modulation, signal processing and frequency shifting of light beams.

9.11 KEY WORDS

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- **Electro-optic effect:** An electro-optic effect is a change in the optical properties of a material in response to an electric field that varies slowly compared with the frequency of light. The term encompasses a number of distinct phenomena, which can be subdivided into some important segments as change of the absorption and change of the refractive index and permittivity.
- **Pockel's effect:** Pockel's effect, also known as the linear electro-optic effect, the birefringence is proportional to the electric field.
- **Kerr effect:** The Kerr effect, also called the Quadratic Electro-Optic (QEO) effect, is a change in the refractive index of a material in response to an applied electric field.
- **Second harmonic generators:** Second-Harmonic Generator (SHG, also called frequency doubling) is a nonlinear optical process in which two photons with the same frequency interact with a nonlinear material, are 'Combined', and generate a new photon with twice the energy of the initial photons (equivalently, twice the frequency and half the wavelength), that conserves the coherence of the excitation.
- **Acousto-optic effect:** Acousto-optics is a branch of physics that studies the interactions between sound waves and light waves, especially the diffraction of laser light by ultrasound (or sound in general) through an ultrasonic grating.

9.12 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the electro-optic effect.
2. Elaborate on the Pockel's effect.
3. Analyse the kerr effect.
4. Explain the second harmonic generators.
5. Write the State of electro-optic modulators.
6. What is the photorefractive materials?
7. Write the acousto-optic effect.

Long-Answer Questions

1. Briefly explain about the electro-optic effect.
2. Explain the Pockel's effect with the examples.

3. Describe the kerr effect and explain its utilisation.
4. Analyse the second harmonic generators and give its applications.
5. What do you mean by electro-optic modulators?
6. Elaborate on the photorefractive materials.
7. Discuss about the acousto-optic effect.

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BLOCK - IV
COMPOSITE AND SMART MATERIALS

UNIT 10 COMPOSITE MATERIAL

Structure

10.0 INTRODUCTION

A composite material (also called a composition material or shortened to composite, which is the common name) is a material which is produced from two or more constituent materials. These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements. Within the finished structure, the individual elements remain separate and distinct, distinguishing composites from mixtures and solid solutions. There are various reasons where new material can be favoured. Typical examples include materials which are less expensive, lighter or stronger when related to common materials. More recently researchers have also begun to actively include sensing, actuation, computation and communication into composites, which are known Composite materials are generally used for buildings, bridges, and structures such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops. The earliest composite materials were made from straw and mud combined to form bricks for building construction. Ancient brick-making was documented by Egyptian tomb paintings Wattle and daub is one of the oldest composite materials, at over 6000 years old. Concrete is also a composite material, and is used more than any other synthetic material in the world. As of 2006, about 7.5 billion cubic metres of concrete are made each year-more than one cubic metre for every person on Earth. Concrete is the most common artificial composite

material of all and typically consists of loose stones (aggregate) held with a matrix of cement. Concrete is an inexpensive material, and will not compress or shatter even under quite a large compressive force. However, concrete cannot survive tensile loading (i.e., if stretched it will quickly break apart). Therefore, to give concrete the ability to resist being stretched, steel bars, which can resist high stretching forces, are often added to concrete to form reinforced concrete. Fibre-reinforced polymers include carbon fibre reinforced polymer and glass-reinforced plastic. If classified by matrix then there are thermoplastic composites, short fibre thermoplastics, long fibre thermoplastics or long fibre-reinforced thermoplastics. There are numerous thermoset composites, including paper composite panels. Many advanced thermoset Polymer Matrix systems usually incorporate aramid fibre and carbon fibre in an epoxy resin matrix. Carbon composite is a key material in today's launch vehicles and heat shields for the re-entry phase of spacecraft. It is widely used in solar panel substrates, antenna reflectors and yokes of spacecraft. It is also used in payload adapters, inter-stage structures and heat shields of launch vehicles. Furthermore, disk brake systems of airplanes and racing cars are using carbon/carbon material, and the composite material with carbon fibres and silicon carbide matrix has been introduced in luxury vehicles and sports cars. The major benefit of these advanced composite materials is that they are lightweight as well as carry high building strength. By selecting the appropriate recipe of the matrix and reinforcement materials, the new material can be designed that precisely meets the necessities of a specific application. Composites can also be designed.

In various ways because most of the composites can be molded into complex shapes. Sometimes the costs of the raw materials are high which makes it hard to use such composite materials at all places.

In this unit, you will study about the Polymer-Matrix composites, cement - matrix composites, carbon-matrix composites, Metal-Matrix composites, Ceramic-Matrix composites.

10.1 OBJECTIVES

After going through this unit, you will be able to:

- Describe of composite material
- Explain the polymer-matrix composite
- Understand the cement-matrix composite
- Elaborate the carbon-matrix composite
- Discuss about the metal-matrix composite and its application
- Analyses the ceramic-matrix composite

10.2 COMPOSITE MATERIAL: AN INTRODUCTION

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The mixing of two materials with different physical and chemical properties forms a composite. In this way, the material is designed to outgrow providing the desired job. Sometimes they become stronger, lighter, or electrically resistant. There are several other benefits to be pointed responsible for the growth of the composite materials but the specific goal achieved by the composites is that they are stronger in strength and lighter in weight. The utilization of composite materials is widespread and connected to almost all the industries we can think of. With the industrial advancements in time, in the past four decades, the conventional building materials were replaced by advanced materials designed for specific applications. In general, the industries of composite materials can be classified into the following categories: construction, marine corrosion-resistant equipment, aerospace, automotive, consumer products, appliance/business equipment, etc.

Whereas, the materials available can be divided into these categories: polymers, ceramics, metals, and inorganic glasses and composites. Generally, metals weaken in their strength as the ambient temperature increases. Several polymers can only bear a low temperature. Ceramics surpass polymers and metals because of their ability to bear high temperatures, excellent mechanical strength, and low thermal expansion, but they are brittle which becomes the reason for its rejection from being a structural material. All these points converge to a common need for composite materials.

The development of strong reinforcements like carbon fiber together with advances in polymer research to harvest high-performance resins as matrix materials. The polymer network materials have helped to meet the challenges caused by the design complexities of recent aircrafts. The development of helicopters, satellites, military fighter aircraft, small, big civil transport aircraft, launch vehicles, and missiles is the most suitable example of the utilization of the potential of such composite materials.

The major benefit of these advanced composite materials is that they are lightweight as well as carry high building strength. By selecting the appropriate recipe of the matrix and reinforcement materials, the new material can be designed that precisely meets the necessities of a specific application. Composites can also be designed in various ways because most of the composites can be molded into complex shapes. Sometimes the costs of the raw materials are high which makes it hard to use such composite materials at all places.

10.3 POLYMER-MATRIX COMPOSITE

The automobile industry has been flourished by the structural applications of E-glass fiber. Likewise, resin systems are most expected to dominate in recent times. High-performance resins will be used for its specific application. The glass

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fiber foam is also of very specific use, and both continuous and chopped glass fibers are of wide-ranging use. Most structural applications dealing with heavy loads use a mixture of both continuous and chopped glass fibers with the specific quantities of each depending upon the structure.

Advanced composites and reinforced plastics are two main categories of Polymer Matrix Composite (PMC). The mechanical properties such as strength and stiffness of these materials are the basis of this classification. Otherwise, the difference between them is defined quite clearly. Comparatively inexpensive reinforced plastics, generally carry polyester resins are reinforced with low-stiffness glass fibers. Being light weight is the main advantage of PMCs along with this they have good strength in the direction of the reinforcement. Such a combination of properties is the reason for their usefulness. Besides, these materials demonstrate excellent fatigue and corrosion resistance in comparison to metals. The only drawback is that the matrix decomposes at high temperatures, so, the PMCs can only be used up to 600 °F (316 °C).

Applications of Polymer-Matrix Composite

The automotive industry is a big scope for all such material research advancements. The multiple places of utility accommodate many advanced composite materials, PMCs are one of them. PMCs provide light weight and good strength material thus the efficiency of the automobiles can be increased. Along with this, its corrosion resistance nature makes it durable to use for several applications. The development in this field of materials would have a significant impact on new ways of its production, and it will also emerge some new industries. The benefits of advanced materials to automotive structures requires:

1. Long-term effects on the PMC structures and the clear evidence of the performance capabilities of PMC based materials.
2. The growth of reliable manufacturing units to produce PMCs at high speed with quality control.
3. The manufacturing-dependent economic incentives should be provided.

The criteria of performance applicable to new materials like PMCs in automotive are

1. Fatigue (durability)
2. Energy absorption (during accident)
3. Material stiffness in terms of ride quality, vibration, and noise

Modern-day Research and Development (R&D) is pointed at realizing eight potential benefits of PMC structures for the automotive industry:

1. Reduction of weight, which on the other side makes vehicle fuel economy and enhances its performance.

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2. Overall improvement in built quality and uniformity in manufacturing.
3. The reduction of overall manufacturing costs.
4. Improvement in ride performance (such as, reduced noise, and lesser vibrations).
5. Automotive-style differentiation with acceptable or reduced cost.
6. Lower investments for the establishment of its plant, facilities, and research and development.
7. Resistance towards corrosion.

10.4 CEMENT-MATRIX COMPOSITES

Cement plays the role of a binder in concrete. The cement matrix gains its shape during the hydration process and binds the components together. The quantity of cement in concrete is limited but its presence controls most concrete properties. Cement composites are a very important part of civil infrastructure. The incorporation of carbon fibers, nanotubes, or nanofibers in cement-matrix provides functionalities above the structural application due to their electrical conductivity. Cement-matrix composite materials consist of hardened cement paste, which is formed by the hydration process between cement and the water, and sometimes a mixture of various inorganic, metallic, or polymeric materials. The mixture of all three types of materials mentioned above.

Check Your Progress

1. What is composite material?
2. Write the benefits of composite materials.
3. Define the criteria of performance of Polymer-Matrix Composites or PMCs in automotive.
4. Explain the role of cement-matrix composite.

10.5 CARBON-MATRIX COMPOSITES

Carbon fibers embedded in a carbonaceous matrix forms a special kind of composite called carbon-carbon composite. Carbon is an excellent material that persists even up to high temperatures when used in inert or non-oxidizing atmospheres. The major with carbon is that it easily reacts with oxygen, forming oxides. Carbon-carbon composite materials are commercially very useful. Heat shields, heating elements, load plates, and X-ray targets are made using this material. The nozzle of a rocket exhaust must bear an extremely rapid increase in temperature in a highly corrosive environment while sustaining its strength. This is a fascinating

material used in many applications in the field of aerospace technology, wind energy production, automotive engineering, mechanical engineering, medical technology, and the sports industry.

Carbon composites have a wide range of advantages such as:

- Extremely light weight
- Long-lasting
- Non-corrosive
- Multifunctional
- High stability
- High energy absorption in an accident
- Attractive looks

Applications of Carbon-Matrix Composites

- High-performance braking system
- Turbojet engine components (rocket nozzles)
- Hot-press die
- Refractory material (protection tubes and grids)
- Heating elements

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10.6 METAL-MATRIX COMPOSITES

Metal-Matrix Composites (MMCs), are not used as much as their plastic opponents, irrespective of their vital interest in research groups. These materials offer high strength, and toughness comparative to those presented by their polymer counterparts. They can bear high temperatures with much comfort rather than polymer composites. The non-reactive and highly stable over a range of temperature reinforcement materials are required to combine with a matrix usually made up of any metal or alloy. The matrix material decides the guiding aspects of the structure of the matrix. Light metals are used to form the matrix for temperature applications and the reinforcement material in addition to the above-mentioned reasons are categorized by the high modulus of rigidity. Most metals and alloys make good matrices. But it cannot be used for low-temperature applications. The use of light metals is advantageous in the manufacturing of these materials. The metals such as aluminum, titanium, and magnesium are the popular matrix metals presently being explored. These light metals are specifically useful for their application in aircraft industries if matrix materials are made up of light materials and offer high strength. The high value of strength-to-weight ratios is required for these properties. Most ceramics, metals, and compounds can be used with these matrices of lower melting points. The selection of reinforcement material becomes more important with the increasing melting points of matrix materials.

Advantages: MMC is more preferred over Polymer-Matrix Composites (PMCs) which can be operated at higher temperatures, and have greater resistance to degradation caused by organic fluids. Whereas, higher cost of MMCs over PMCs restricts their use to some extent.

Constitution: The matrix-materials cover super alloys as well as the alloys of magnesium, titanium, aluminum, and copper. The reinforcement can be in the form of both continuous and discontinuous fibers. Whose concentration normally ranges between 10 to 60 %vol. materials containing continuous fibers comprise carbon, aluminum oxide, silicon carbide, and boron. Instead, silicon carbide whiskers, chopped fibers of aluminum oxide and carbon, and particulates of silicon carbide and aluminum oxide are some vital discontinuous reinforcements.

Application

In the field of automobile production: the aluminum alloy matrix that is used as reinforcement consists of aluminum oxide and carbon fibers. This is used to form the main engine components. This MMC resists wear and very light in weight. These composites are also used in driveshafts as they required high rotational speed and reduced vibrational noise levels. On the other hand, in the aerospace industry: advanced aluminum alloy-based Metal-Matrix composites are formed for structural requirements; Space Shuttle Orbiters are constructed using boron fibers as a reinforcer. In the Hubble space telescope, continuous graphite fibers were used as a reinforcer.

The high-temperature creeps and rupture properties of some of the Ni-based and Co-based super alloys are enhanced by means of fiber reinforcement using tungsten like refractory metals. Excellent impact strength and oxidation resistance at high temperatures are maintained. The designs consisting of these composites permit better efficiencies and higher operating temperatures for turbine engines.

10.7 CERAMIC-MATRIX COMPOSITES

Ceramic materials are defined as solid materials exhibiting strong ionic bonding and covalent bonding in some cases. They usually have a high melting point, good resistance towards corrosion, and high inertness for chemicals. These materials also possess high compressive strength. That is the reason why ceramic-based matrix materials are favorite for structural applications above a temperature of 1500 ºC. In general, Ceramic Matrix materials are the obvious choice at elevated temperatures. Low tensile strain and high modulus of elasticity are possessed by the ceramics. These properties in combination became the reason for unsuccess in the attempts to add reinforcements in these materials to improve its material strength. This may happen because the stress level at which a ceramic breaks, the elongation of the matrix is not sufficient; which does not allow the composite from transferring the load to the reinforcement and it fails until there is a sufficiently high percentage

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of fiber present in the material. On the other hand, the addition of a heavy quantity of high-strength fiber weakens the ceramic most of the time. The reinforcement can be used in a material with a high modulus of elasticity. It may work to some extent but not always. Ceramic materials are inherently resistant to oxidation and degradation at high temperatures. Some of these materials would be ideal for use in high temperature and stress conditions, especially in aircraft engines and heat portions in automobiles. The values of fracture toughness for these ceramic materials are not that high and generally lies between 1 to 5 MPa. On the other hand, these values are very high for metals of the order of 15 to 150 or sometimes even more in MPa. Ceramic-Matrix Composites (CMCs) are formed to increase the fracture toughness of these materials. In these materials, fibers, particulates, or whiskers of one ceramic material are embedded into the matrix formed by another ceramic. The facture toughness of CMCs has been extended about 6 to 20 MPa.

Applications of CMCs

CMCs find applications in many industrial applications. A suitable organization of the applications of Ceramic Matrix Composites (CMCs) is aerospace and non-aerospace. CMCs used in the field of aerospace are:

- High stiffness and better material strength.
- Reduction in weight, and, lesser fuel consumption as a consequence.
- Lower maintenance and fabrication cost.
- Highly thermal resistant.
- Longer service life.
- Valuable in stealth technology (reduces the distance at which a vehicle can be detected).

Check Your Progress

5. Explain the application of carbon-matrix composite.
6. Write the performance of metal-matrix composite at high temperature.
7. Give the advantages of metal-matrix composite.
8. What is ceramic-matrix composite?

10.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The mixing of two materials with different physical and chemical properties forms a composite. In this way, the material is designed to outgrow providing the desired job. Sometimes they become stronger, lighter, or electrically resistant.

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2. The major benefit of these advanced composite materials is that they are lightweight as well as carry high building strength. By selecting the appropriate recipe of the matrix and reinforcement materials, the new material can be designed that precisely meets the necessities of a specific application. Composites can also be designed in various ways because most of the composites can be molded into complex shapes. Sometimes the costs of the raw materials are high which makes it hard to use such composite materials at all places.
3. The criteria of performance applicable to new materials like PMCs in automotive are:
   (i) Fatigue (durability)
   (ii) Energy absorption (during accident)
   (iii) Material stiffness in terms of ride quality, vibration, and noise
4. Cement plays the role of a binder in concrete. The cement matrix gains its shape during the hydration process and binds the components together. The quantity of cement in concrete is limited but its presence controls most concrete properties.
5. Applications of Carbon-Matrix Composites
   - High-performance braking system
   - Turbojet engine components (rocket nozzles)
   - Hot-press die
   - Refractory material (protection tubes and grids)
   - Heating elements
6. Metal-Matrix Composites (MMCs), are not used as much as their plastic opponents, irrespective of their vital interest in research groups. These materials offer high strength, and toughness comparative to those presented by their polymer counterparts.
7. MMC is more preferred over Polymer-Matrix Composites (PMCs) which can be operated at higher temperatures, and have greater resistance to degradation caused by organic fluids. Whereas, higher cost of MMCs over PMCs restricts their use to some extent.
8. Ceramic materials are defined as solid materials exhibiting strong ionic bonding and covalent bonding in some cases. They usually have a high melting point, good resistance towards corrosion, and high inertness for chemicals. These materials also possess high compressive strength.

10.9 SUMMARY

- The mixing of two materials with different physical and chemical properties forms a composite. In this way, the material is designed to outgrow providing

the desired job. Sometimes they become stronger, lighter, or electrically resistant.

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- The utilization of composite materials is widespread and connected to almost all the industries we can think of. With the industrial advancements in time, in the past four decades, the conventional building materials were replaced by advanced materials designed for specific applications.
- In general, the industries of composite materials can be classified into the following categories: construction, marine corrosion-resistant equipment, aerospace, automotive, consumer products, appliance/business equipment, etc.
- The materials available can be divided into these categories: polymers, ceramics, metals, and inorganic glasses and composites.
- Ceramics surpass polymers and metals because of their ability to bear high temperatures, excellent mechanical strength, and low thermal expansion, but they are brittle which becomes the reason for its rejection from being a structural material. All these points converge to a common need for composite materials.
- The polymer network materials have helped to meet the challenges caused by the design complexities of recent aircrafts. The development of helicopters, satellites, military fighter aircraft, small, big civil transport aircraft, launch vehicles, and missiles is the most suitable example of the utilization of the potential of such composite materials.
- The major benefit of these advanced composite materials is that they are lightweight as well as carry high building strength. By selecting the appropriate recipe of the matrix and reinforcement materials, the new material can be designed that precisely meets the necessities of a specific application. Composites can also be designed in various ways because most of the composites can be molded into complex shapes. Sometimes the costs of the raw materials are high which makes it hard to use such composite materials at all places.
- The automobile industry has been flourished by the structural applications of E-glass fiber. Likewise, resin systems are most expected to dominate in recent times. High-performance resins will be used for its specific application.
- The glass fiber foam is also of very specific use, and both continuous and chopped glass fibers are of wide-ranging use. Most structural applications dealing with heavy loads use a mixture of both continuous and chopped glass fibers with the specific quantities of each depending upon the structure.
- The automotive industry is a big scope for all such material research advancements. The multiple places of utility accommodate many advanced composite materials, PMCs are one of them. PMCs provide light weight and good strength material thus the efficiency of the automobiles can be increased.

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- Cement plays the role of a binder in concrete. The cement matrix gains its shape during the hydration process and binds the components together. The quantity of cement in concrete is limited but its presence controls most concrete properties.
- Cement composites are a very important part of civil infrastructure. The incorporation of carbon fibers, nanotubes, or nanofibers in cement-matrix provides functionalities above the structural application due to their electrical conductivity.
- The major with carbon is that it easily reacts with oxygen, forming oxides. Carbon/carbon composite materials are commercially very useful. Heat shields, heating elements, load plates, and X-ray targets are made using this material.
- Carbon composites have a wide range of advantages such as:
  - o Extremely light weight
  - o Long-lasting
  - o Non-corrosive
  - o Multifunctional
  - o High stability
  - o High energy absorption in an accident
  - o Attractive looks
- Metal-Matrix Composites (MMCs), are not used as much as their plastic opponents, irrespective of their vital interest in research groups. These materials offer high strength, and toughness comparative to those presented by their polymer counterparts.
- High temperatures with much comfort rather than polymer composites. The non-reactive and highly stable over a range of temperature reinforcement materials are required to combine with a matrix usually made up of any metal or alloy.
- Light metals are used to form the matrix for temperature applications and the reinforcement material in addition to the above-mentioned reasons are categorized by the high modulus of rigidity.
- MMC is more preferred over Polymer-Matrix Composites (PMCs) which can be operated at higher temperatures, and have greater resistance to degradation caused by organic fluids. Whereas, higher cost of MMCs over PMCs restricts their use to some extent.
- Ceramic materials are defined as solid materials exhibiting strong ionic bonding and covalent bonding in some cases. They usually have a high melting point, good resistance towards corrosion, and high inertness for chemicals. These materials also possess high compressive strength.

- The addition of a heavy quantity of high-strength fiber weakens the ceramic most of the time. The reinforcement can be used in a material with a high modulus of elasticity.

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10.10 KEY WORDS

- **Composite:** The mixing of two materials with different physical and chemical properties forms a composite.
- **Cement-matrix composite:** Cement-matrix composite materials consist of hardened cement paste, which is formed by the hydration process between cement and the water, and sometimes a mixture of various inorganic, metallic, or polymeric materials.
- **Carbon-carbon composite:** Carbon fibers embedded in a carbonaceous matrix forms a special kind of composite called carbon-carbon composite. Carbon is an excellent material that persists even up to high temperatures when used in inert or non-oxidizing atmospheres.
- **Metal-Matrix Composites (MMCs):** These materials offer high strength, and toughness comparative to those presented by their polymer counterparts. They can bear high temperatures with much comfort rather than polymer composites.
- **Ceramic materials:** Ceramic materials are defined as solid materials exhibiting strong ionic bonding and covalent bonding in some cases. They usually have a high melting point, good resistance towards corrosion, high inertness for chemicals and high compressive strength. That is the reason why ceramic-based matrix materials are favourite for structural applications above a temperature of 1500 ºC.

10.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the benefits of composite materials.
2. Why the composite materials are used?
3. Give the applications of polymer-matrix composites.
4. What is cement-matrix composite?
5. Elaborate on the term carbon-matrix composite.
6. Explain about the metal-matrix composite.
7. What are constituent of metal-matrix material?
8. Write short note on ceramic-matrix composite.

Long-Answer Questions

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1. Discuss briefly about the composite materials and its uses with the help of examples.
2. Elaborate on the polymer-matrix composites and its applications with the help of appropriate examples.
3. Briefly explain about the cement-matrix composites giving appropriate examples.
4. Explain about the carbon-matrix composite with their advantages and applications.
5. Explain in detail about the metal-matrix composites with their advantages, constituents and applications.
6. Discuss briefly about the ceramic-matrix composites and its applications giving appropriate examples.

10.12 FURTHER READINGS

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UNIT 11 APPLICATIONS OF COMPOSITE MATERIALS

Structure

11.0 INTRODUCTION

A composite material (also called a composition material or shortened to composite, which is the common name) is a material which is produced from two or more constituent materials. These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements. Within the finished structure, the individual elements remain separate and distinct, distinguishing composites from mixtures and solid solutions.

There are various reasons where new material can be favoured. Typical examples include materials which are less expensive, lighter or stronger when related to common materials. More recently researchers have also begun to actively include sensing, actuation, computation and communication into composites, which are known as Robotic Materials. Composite materials are generally used for buildings, bridges, and structures such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.

The most advanced examples perform routinely on spacecraft and aircraft in demanding environments. The earliest composite materials were made from straw and mud combined to form bricks for building construction. Ancient brick-making was documented by Egyptian tomb paintings. Wattle and daub is one of the oldest composite materials, at over 6000 years old. Concrete is also a composite material, and is used more than any other synthetic material in the world. As of 2006, about 7.5 billion cubic metres of concrete are made each year-more than one cubic metre for every person on Earth.

In this unit, you will study about the applications and structure of composite material, such as electronics, thermal, electrochemical, environmental, biomedical.

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11.1 OBJECTIVES

After going through this unit, you will be able to:

- Elaborate on the important and structure of composite material
- Understand the significance of electronics uses composite materials
- Explain about the thermal applications composite materials
- Analyse the electrochemical features composite materials
- Discuss the environmental specifications of composite materials
- Analyse the biomedical feature of composite materials

11.2 APPLICATIONS OF DIFFERENT TYPES OF COMPOSITE MATERIALS

Applications of Composite Materials

A composite material (also called a composition material or shortened to composite, which is the common name) is a material which is produced from two or more constituent materials. These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements. Within the finished structure, the individual elements remain separate and distinct, distinguishing composites from mixtures and solid solutions.

Typical engineered composite materials include:

- Reinforced concrete and masonry
- Composite wood such as plywood
- Reinforced plastics, such as fibre-reinforced polymer or fiberglass
- Ceramic matrix composites (composite ceramic and metal matrices)
- Metal matrix composites
- And other advanced composite materials

Applications of Different Types of Composite Materials

There are various reasons where new material can be favoured. Typical examples include materials which are less expensive, lighter or stronger when related to common materials.

More recently researchers have also begun to actively include sensing, actuation, computation and communication into composites, which are known as Robotic Materials.

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Composite materials are generally used for buildings, bridges, and structures such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.

The most advanced examples perform routinely on spacecraft and aircraft in demanding environments.

Carbon composite is a key material in today's launch vehicles and heat shields for the re-entry phase of spacecraft. It is widely used in solar panel substrates, antenna reflectors and yokes of spacecraft. It is also used in payload adapters, inter-stage structures and heat shields of launch vehicles. Furthermore, disk brake systems of airplanes and racing cars are using carbon/carbon material, and the composite material with carbon fibres and silicon carbide matrix has been introduced in luxury vehicles and sports cars.

Concrete is the most common artificial composite material of all and typically consists of loose stones (aggregate) held with a matrix of cement. Concrete is an inexpensive material, and will not compress or shatter even under quite a large compressive force. However, concrete cannot survive tensile loading (, i.e., if stretched it will quickly break apart). Therefore, to give concrete the ability to resist being stretched, steel bars, which can resist high stretching forces, are often added to concrete to form reinforced concrete.

Many commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, PEEK, and others. The reinforcement materials are often fibres but also commonly ground minerals. The various methods described below have been developed to reduce the resin content of the final product, or the fibre content is increased. As a rule of thumb, lay up results in a product containing 60% resin and 40% fibre, whereas vacuum infusion gives a final product with 40% resin and 60% fibre content. The strength of the product is greatly dependent on this ratio.

11.2.1 Electronics Application of Composite Materials

Definition: Composite material is basically a combination of two or more materials, each of which retains its own distinctive properties.

Multiphase metals are composite materials on a micro scale, but generally the term composite is applied to materials that are created by mechanically bonding two or more different materials together. The resulting material has characteristics that are not characteristic of the components in isolation. Most commonly, composite materials have a bulk phase, which is continuous, termed as the **matrix**; and a dispersed, non-continuous, phase termed as the **reinforcement**. Some other examples of basic composites include concrete (cement mixed with sand and aggregate), reinforced concrete (steel rebar in concrete), and fiberglass (glass

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strands in a resin matrix), reinforced concrete (steel rebar in concrete), and fiberglass (glass strands in a resin matrix).

Structure of Composite Materials

The structure of composite material can be categorised as continuous phase and discontinuous phase. The continuous phase is the matrix, which is a polymer, metal, or ceramic. Polymers have low strength and stiffness, metals have intermediate strength and stiffness but high ductility, and ceramics have high strength and stiffness but are brittle. The matrix (continuous phase) performs several critical functions, including maintaining the fibers in the proper orientation and spacing and protecting them from abrasion and the environment. In polymer and metal matrix composites that form a strong bond between the fiber and the matrix, the matrix transmits loads from the matrix to the fibers through shear loading at the interface. In ceramic matrix composites, the objective is often to increase the toughness rather than the strength and stiffness; therefore, a low interfacial strength bond is desirable.

Figure 11.1 shows the highest strength and modulus are obtained with continuous fiber composite.

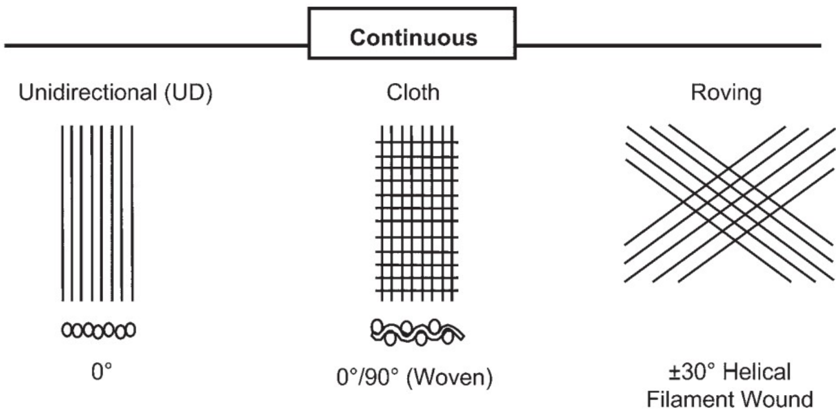


Fig. 11.1 *Continuous Fiber Composites*

Discontinuous fiber composites are normally somewhat random in alignment, which dramatically reduces their strength and modulus. However, the discontinuous fiber composites are generally much less costly as compared to the continuous fiber composites. Figure 11.2 shows the discontinuous fiber composites.

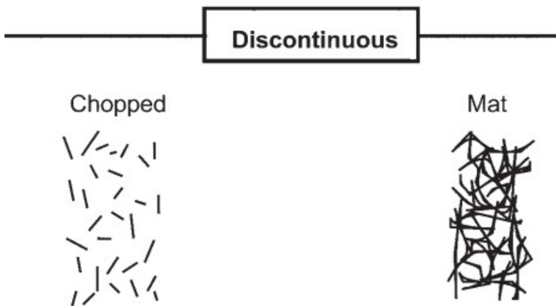


Fig. 11.2 *Discontinuous Fiber Composites*

Advanced composite materials are ideal for electrical and electronic applications because of their high dielectric strength and arc resistance properties.

In combination with a raised continuous operating temperature, progressive composite materials are ideal to act for a wide range of electrically insulation applications.

CME (Composite Material Electronic) thermoset materials provide maximum fire protection using environmentally friendly mineral compounds. Advanced composites are stable through a wide range of operating temperatures varying from as low as –40°C to +60°C and even more using developed compound and moulding techniques and speciality formulations.

CME formulates SMC to the customised standards and with the design freedom available, are ideal for applications demanding ex-proof performance.

With the capability to customise formulations, CME has proven success in supplying components that are required to operate in other aggressive environments. Including frequent temperature loads, outdoor exposure, rough weather conditions, anti-static and chemical attack. Offshore exploration rigs and mining environments are the most challenging examples. Most common applications are lamp housings, terminal boxes, electrical enclosures, plugs, sockets and components for distribution of energy.

More intricate and compact designs, constantly increasing material requirements and cost constraints, will make the use of our material even more compelling in the future.

Benefits of Unconventional Composites

Strong, durable – long life under even extreme weather exposure

Lightweight – easy to transport and install

Reinforcement offer superior sidewall strength

UV protection

Fire retardant with non-toxic smoke

Fast turn – up on production

Weight Reduction

Dimensional Stability

CME Value Additional Facilities

Materials formulated for U.V- stability, stain-resistance

Engineering and design support

Prototyping

Tool Design and construction

11.2.2 Thermal Application of Composite Materials

Effective transfer of heat by conduction requires materials (, such as a heat sink material) of high thermal conductivity. In addition, it requires a good thermal contact between the two surfaces (such as the surface of a heat sink and the surface of a printed circuit board) across which heat transfer occurs. Without good thermal contacts, the use of expensive thermal conducting materials for the components is not cost effective. The attainment of a good thermal contact requires a thermal interface material, such as a thermal grease, which must be thin (small in thickness) between the mating surfaces, must conform to the topography of the mating surface and preferably should have a high thermal conductivity as well. This chapter addresses materials for thermal conduction, including materials of high thermal conductivity and thermal interface materials.

11.2.3 Electrochemical Application of Composite Materials

Electrochemical behaviour relates to chemical procedures brought about by the movement of charged species (ions and electrons) under the impact of an electric field. It occurs when there are ions that can move in a medium (liquid or solid) due to an electric field (i.e., a voltage gradient). The positive ions (cations) move toward the negative end of the voltage gradient, while the negative ions (anions) move toward the positive end of the voltage gradient .The medium encompassing the movable ions is called the *electrolyte* The electrical conductors in contact with the electrolyte for the purpose of applying the electric field are called electrodes. The electrode at the positive end of the voltage gradient is called the *positive electrode or anode* the electrode at the negative end of the voltage gradient is called the *negative electrode or cathode*. The electrodes must be sufficiently inert so that they do not react with the electrolyte. In order to apply the electric field, the electrodes are connected to a DC power supply (or a battery) such that the cathode is linked to the negative end of the power supply (so that the cathode becomes negative) and the anode is connected to the positive end of the battery (so that the anode becomes positive). In this way, electrons flow in the electrical leads (the outer circuit) from the anode to the cathode, while ions flow in the electrolyte. The electron flow in the outer circuit and the ion flow in the electrolyte constitute a loop of charge flow. Note that the anions flow from cathode to anode in the electrolyte, while the electrons flow after anode to cathode in the external circuit and mutually anions and electrons are negatively charged.

11.2.4 Environmental Application of Composite Materials

Biocomposites can supplement and eventually replace petroleum-based composite materials in several applications. Several serious issues related to bio-fibre surface behaviours is to make it an additional appropriate matrix for composite application and promising techniques need to be solved to design specific biocomposite of interest.

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The main motivation for developing biocomposites has been and still is to create a new generation of fibre reinforced plastics material competitive with glass fibre reinforced ones which are ecologically compatible in terms of products, use and renewal. There is a huge opportunity in developing new bio based products, but the real challenge is to design suitable bio-based products through innovation ideas.

Green materials are the wave of the future. Bio-nanocomposites have very strong future prospects, though the present low level of production, some deficiency in technology and high cost restrict them from a wide range of applications.

11.2.5 Biomedical

In material science, the term 'Composite' refers to the combination of two or more materials, which have different composition, morphology and general physical properties. Based on the properties of constituent, the composites can be typically designed to specifically produce materials having properties to fulfil precise specified chemical, physical or mechanical requirements. Consequently over the past 40 years the usage of composite materials has gradually increased, and nowadays composite materials are typically used for several different applications, such as aeronautic, automotive and locomotive, marine (naval), and so on. Subsequently several composite biomaterials have been developed, studied and tested for various medical applications. Maximum human tissues, such as bones, tendons, skin, ligaments, teeth, etc., are composite materials which are exceptionally made up of single constituents whose amount, distribution, morphology and properties determine the final behaviour of the resulting tissue or organ.

Biomedical composites have also been examined for different orthopaedic applications including bone fracture repair, total joint replacement (for hip, knee, etc.) and repair of connective tissues, such as tendon and ligament.

The need for new materials to substitute injured or damaged part of the human body has led scientists of different areas to investigate biomaterials.

Because of the continuous and ever expanding practical needs of medicine and health care practice, there are currently thousands of medical devices, diagnostic products and disposables in the market. In addition to this, the list of biomaterial applications includes tissue cultures, engineered tissues, hybrid organs and smart delivery system for drugs. The application of biomaterials is not limited only to the medical field but also has applications in the industrial field too.

Significant advances have been made in the development of biocompatible and biodegradable materials for biomedical applications. Undoubtedly, biomaterials have had a major impact on the practice of contemporary medicine and patient care in both saving and improving the quality of human and animal lives.

A biomaterial is a substance that has been engineered to interact with biological systems for a medical purpose, either a therapeutic (treat, augment, repair, or replace a tissue function of the body) or a diagnostic one.

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Biomaterials can be derived either from nature or synthesized in the laboratory using a variety of chemical approaches utilizing metallic components, polymers, ceramics or composite materials. They are often used and/or adapted for a medical application, and thus comprise whole or part of a living structure or biomedical device which performs, augments, or replaces a natural function. Such functions may be relatively passive, like being used for a heart valve, or maybe bioactive with a more interactive functionality, such as hydroxy-apatite coated hip implants. Biomaterials are also used every day in dental applications, surgery, and drug delivery. For example, a construct with impregnated pharmaceutical products can be placed into the body, which permits the prolonged release of a drug over an extended period of time. A biomaterial may also be an autograft, allograft or xenograft used as a transplant material.

Biopolymers are polymers produced by living organisms. Cellulose and starch, proteins and peptides, and DNA (DeoxyriboNucleic Acid) and RNA (RiboNucleic Acid) are all examples of biopolymers, in which the monomeric units, respectively, are sugars, amino acids, and nucleotides. Cellulose is both the most common biopolymer and the most common organic compound on Earth. About 33% of all plant matter is cellulose. On a similar manner, silk (proteinaceous biopolymer) has garnered tremendous research interest in a myriad of domains including tissue engineering and regenerative medicine, microfluidics, drug delivery.

Check Your Progress

1. Define the term composite materials.
2. Explain about the uses of composite materials.
3. Elaborate on the electronic behaviour of composite materials.
4. What do you understand by the thermal feature of composite materials?
5. What is the electrochemical nature of composite materials?

11.3 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. A composite material (also called a composition material or shortened to composite, which is the common name) is a material which is produced from two or more constituent materials. These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements.
2. Composite materials are generally used for buildings, bridges, and structures, such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.

3. CME (Composite Material Electronic) thermoset materials provide maximum fire protection using environmentally friendly mineral compounds. Advanced composites are stable through a wide range of operating temperatures varying from as low as -40°C to +60°C and even more using developed compound and moulding techniques and speciality formulations.
4. Effective transfer of heat by conduction requires materials (such as, a heat sink material) of high thermal conductivity. In addition, it requires a good thermal contact between the two surfaces (such as, the surface of a heat sink and the surface of a printed circuit board) across which heat transfer occurs.
5. Electrochemical behaviour relates to chemical procedures brought about by the movement of charged species (ions and electrons) under the impact of an electric field. It occurs when there are ions that can move in a medium (liquid or solid) due to an electric field (i.e., a voltage gradient).

11.4 SUMMARY

- A composite material (also called a composition material or shortened to composite, which is the common name) is a material which is produced from two or more constituent materials. These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements.
- More recently researchers have also begun to actively include sensing, actuation, computation and communication into composites, which are known as Robotic Materials.
- Composite materials are generally used for buildings, bridges, and structures, such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.
- Carbon composite is a key material in today's launch vehicles and heat shields for the re-entry phase of spacecraft. It is widely used in solar panel substrates, antenna reflectors and yokes of spacecraft.
- Carbon composite is also used in payload adapters, inter-stage structures and heat shields of launch vehicles. Furthermore, disk brake systems of airplanes and racing cars are using carbon/carbon material, and the composite material with carbon fibres and silicon carbide matrix has been introduced in luxury vehicles and sports cars.
- Concrete is the most common artificial composite material of all and typically consists of loose stones (aggregate) held with a matrix of cement. Concrete

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is an inexpensive material, and will not compress or shatter even under quite a large compressive force.

- Many commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients.
- The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, PEEK, and others. The reinforcement materials are often fibres but also commonly ground minerals.
- The structure of composite material can be categorised as continuous phase and discontinuous phase. The continuous phase is the matrix, which is a polymer, metal, or ceramic.
- Polymers have low strength and stiffness, metals have intermediate strength and stiffness but high ductility, and ceramics have high strength and stiffness but are brittle.
- Advanced composite materials are ideal for electrical and electronic applications because of their high dielectric strength and arc resistance properties.
- CME (Composite Material Electronic) thermoset materials provide maximum fire protection using environmentally friendly mineral compounds.
- Advanced composites are stable through a wide range of operating temperatures varying from as low as –40°C to +60°C and even more using developed compound and moulding techniques and speciality formulations.
- Effective transfer of heat by conduction requires materials (such as, a heat sink material) of high thermal conductivity. In addition, it requires a good thermal contact between the two surfaces (such as, the surface of a heat sink and the surface of a printed circuit board) across which heat transfer occurs.
- Without good thermal contacts, the use of expensive thermal conducting materials for the components is not cost effective.
- Electrochemical behaviour relates to chemical procedures brought about by the movement of charged species (ions and electrons) under the impact of an electric field. It occurs when there are ions that can move in a medium (liquid or solid) due to an electric field (i.e., a voltage gradient).
- Biocomposites can supplement and eventually replace petroleum-based composite materials in several applications. Several serious issues related to bio-fibre surface behaviours is to make it an additional appropriate matrix for composite application and promising techniques need to be solved to design bio composite of interest.

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- The continuous and ever expanding practical needs of medicine and health care practice, there are currently thousands of medical devices, diagnostic products and disposables in the market. In addition to this, the list of biomaterial applications includes tissue cultures, engineered tissues, hybrid organs and smart delivery system for drugs.
- A biomaterial is a substance that has been engineered to interact with biological systems for a medical purpose, either a therapeutic (treat, augment, repair, or replace a tissue function of the body) or a diagnostic one.
- Biomaterials can be derived either from nature or synthesized in the laboratory using a variety of chemical approaches utilizing metallic components, polymers, ceramics or composite materials. They are often used and/or adapted for a medical application, and thus comprise whole or part of a living structure or biomedical device which performs, augments, or replaces a natural function.
- A biomaterial may also be an autograft, allograft or xenograft used as a transplant material.
- Biopolymers are polymers produced by living organisms. Cellulose and starch, proteins and peptides, and DNA (DeoxyriboNucleic Acid) and RNA (RiboNucleic Acid) are all examples of biopolymers, in which the monomeric units, respectively, are sugars, amino acids, and nucleotides.

11.5 KEY WORDS

- **CME (Composite Material Electronic):** The CME (Composite Material Electronic) thermoset materials provide maximum fire protection using environmentally friendly mineral compounds. Advanced composites are stable through a wide range of operating temperatures varying from as low as –40°C to +60°C and even more using developed compound and moulding techniques and speciality formulations
- **Thermal composite materials:** Effective transfer of heat by conduction requires materials (such as, a heat sink material) of high thermal conductivity. In addition, it requires a good thermal contact between the two surfaces (such as, the surface of a heat sink and the surface of a printed circuit board) across which heat transfer occurs.
- **Electrochemical composite materials:** Electrochemical behaviour relates to chemical procedures brought about by the movement of charged species (ions and electrons) under the impact of an electric field. It occurs when there are ions that can move in a medium (liquid or solid) due to an electric field (i.e., a voltage gradient).

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- **Biocomposite materials:** Biocomposites can supplement and eventually replace petroleum-based composite materials in several applications.
- **Biomaterial:** A biomaterial is a substance that has been engineered to interact with biological systems for a medical purpose, either a therapeutic (treat, augment, repair, or replace a tissue function of the body) or a diagnostic one.
- **Biopolymers:** Biopolymers are polymers produced by living organisms. Cellulose and starch, proteins and peptides, and DNA (DeoxyriboNucleic Acid) and RNA (RiboNucleic Acid) are all examples of biopolymers, in which the monomeric units, respectively, are sugars, amino acids, and nucleotides.

11.6 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the composite materials.
2. Explain features about the electronic of composite materials.
3. Analyse the thermal activity of composite materials.
4. Elaborate on the environmental nature of composite materials.
5. What do you understand by the biomedical applications of composite materials?

Long-Answer Questions

1. Describe briefly the applications and structure of composite materials.
2. Explain about the electronic and thermal nature of composite materials.
3. Explain the electrochemical and environmental behaviour of composite materials.
4. Elaborate on the biomedical applications of the composite materials.

11.7 FURTHER READINGS

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UNIT 12 SMART MATERIALS

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Structure

12.0 INTRODUCTION

Smart materials are a specific kind of materials operated to respond in the desired way, and the move is reversible as well. Some of their properties such as mechanical stress can be modified through external stimulation. The smart materials are also called responsive materials because of their responsiveness towards some external ambient provocations. These materials are also termed active materials although their behaviour suits more accurately by the name reactive material. In a nutshell, these materials react to external provocations and show a change in one or more properties. Smart materials can change shape or behaviours with changes in pressure, hotness, change in a chemical environment,

With the advent of Material Science and Engineering, so many new engineering material have been discovered. The newly discovered engineering materials find major application in industries. In general, the materials are classified as metals and alloys, ceramics, glasses, glass ceramics, composites, polymers and semiconductors.

To design a new engineering material with the required properties for a specific application, low cost and safety factor consideration, a sound knowledge of the structure, properties, processing and composition is required. In the following sections, new engineering materials like metallic glasses, nanomaterials, shape memory alloys and biomaterials are discussed in brief.

Amorphous solids are well known by the definition that the atoms and molecules in an amorphous solid are not organized. Such materials are surrounding us in the form of plastic, gel, and glass. Generally, both solid and liquids have long-range and short-range order of atoms for long and short terms, respectively. Using the term glass means an amorphous material. This is a Greek word that means

something without shape. It also lacks in long-range order of atoms, contrary to the crystalline materials, organized in a defined repeated pattern. A glass results because of the phenomenon of glass transition which is a special kind of transition from the super cooled liquid.

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In this unit, you will study about the amorphous and glassy materials, structure, preparation methods, and novel properties.

12.1 OBJECTIVES

After going through this unit, you will be able to:

- Define the amorphous and glassy material
- Explain the structure of smart material
- Discuss about the preparation method of smart material
- Analyse the important novel properties of smart material

12.2 AMORPHOUS AND GLASSY MATERIALS

Metallic glasses are the newly developed engineering materials. Metallic glasses share the properties of both metals and alloys.

Most metals and alloys are crystalline, i.e., their atoms are arranged in a regular pattern that extends over a long distance. In contrast, a glass is an amorphous (non-crystalline), brittle and transparent solid.

Thus, metallic glasses are the metal alloys that are amorphous. That is, they do not have a long range atomic order. The major advantages of such glasses are that they are generally homogeneous in composition, and offer strong and superior corrosion resistance.

To have this peculiar property, the metallic glasses are to be made by cooling a molten metal rapidly at a rate of 2×10^{60} Cs^{-1}. During this process of solidification, the atoms do not have enough time or energy to rearrange for crystal nucleation. Thus, the liquid upon reaching the glass transition temperature T_g solidifies as a metallic glass. Again, upon heating metallic glasses show a reversible glass-liquid transition at T_g.

Amorphous Materials: Amorphous solids are well known by the definition that the atoms and molecules in an amorphous solid are not organized. Such materials are surrounding us in the form of plastic, gel, and glass. Generally, both solid and liquids have long-range and short-range order of atoms for long and short terms, respectively. The term 'order' used here stands for the proper arrangement of atoms in a repeating form. But in the case of amorphous solids, the material is rarely ordered at some places but mostly being random in the arrangement. These are intermediate materials such that they are jammed

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liquids but show yield stress like solids. These are also known as supercooled liquids. Such materials flow like a fluid under large stress but remain stationary under smaller stresses. They also show complex behavior depending on their histories. Foams, Emulsions and Colloids, and even living tissues are some examples of amorphous materials. Besides, granular materials, bulk metallic glasses, and bubble rafts are some of the disordered materials exhibiting yield stress.

1. **Glass:** Using the term glass means an amorphous material. This is a Greek word that means something without shape. It also lacks in long-range order of atoms, contrary to the crystalline materials, organized in a defined repeated pattern. A glass results because of the phenomenon of glass transition which is a special kind of transition from the super cooled liquid. In this way, it can be added that all the amorphous materials are not glassy solids. This is because they are not formed by this phenomenon. The amorphous nature can be explained as glass is a highly viscous liquid at room temperature. The highly viscous liquid flows like a fluid but the process is very much slow such that It generally remains unnoticed in a human lifespan. Like other fluids, the viscosity of the glass as well changes with the temperature. Four standard temperatures are used while working with the glasses which define their viscosity. These temperatures are termed strain, annealing, softening, and working temperatures. The strain point is the highest temperature at which a glass can be used for several structural applications. Beyond this point, the glass-forming processes are performed between the softening and the working temperatures. The glass yields a small amount of force at the softening temperature. Whereas, at the working temperature, the glass becomes as viscous as honey. Finally, the annealing temperature is the one at which glass relieves all the internal stresses generated because of the processes used for forming and shaping the glass.
2. **Structure of Glass:** As discussed in the above sections, glass is a non-repetitive arrangement of atoms or molecules. The major portion of the glass is made up of oxygen ions bonded with silicon, boron, or phosphorus ions and forming a network. The glass can also be formed using silica only but the involvement of high processing temperature makes it difficult to prepare and expensive as well. Some modifications are done by adding potassium, sodium, or calcium to reduce its processing temperature. These ions are also called network modifying ions. These ions compete with oxygen ions and decrease the strength of Si-O bonds. Therefore, some other ions could be used either for network-forming or network-modification, for example Beryllium, Lead, Aluminium, and Zinc are some intermediate ions.

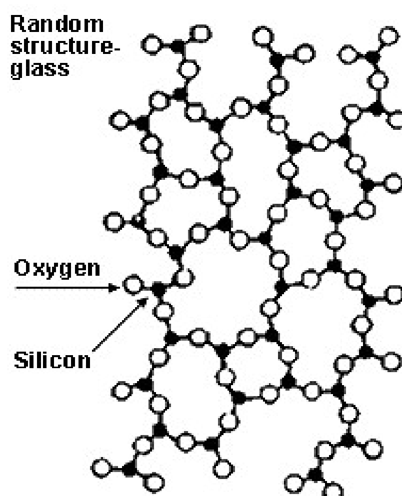


Fig. 12.1 *The Structure of a Glass*

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3. **Types of Glass Based on Functionality**

   a. Smart Glass

   Smart glasses can be defined by modifying the structure of the glass, or technologies that expand the performance of polymer- or glass-based products. These can be implemented through the surface coating, laminated structures with embedded electronic circuits.

   b. Electro-Optic Glass

   Glassy materials that change their optical properties with electrical stimulation can be termed electro-optic glasses. These materials are also known as electrochromic glasses. Chroma is a Greek word that means color and the change in color because of an electronic provocation is the term electrochromic stands for. Some famous examples of such materials are Polymer-Dispersed Liquid Crystals (PDLC), and Suspended-Particle Devices (SPD).

   c. Photo-Optic Glass

   Photo-optic glass is the one that changes color and the effect is stimulated by the photons. Modern-day spectacles are designed in such a way that they become darker in the shade as more sunlight passes through them and photo-optic glasses try to maintain a constant intensity of light for our eyes.

   d. Thermo-Optic Glass

   The thermo-optic glasses show a variation in the refractive index with a temperature change. These materials are also classified as thermo-chromic. As it is trivial from the structure of the word that it deals in the chromic variation with the variation in ambient temperature.

4. **Glass-Making Techniques:** The general techniques used for making glass were well known even in the ancient past. The tools used by the glassmakers

have not been changed much since its discovery. However, other technological advancements such as better electrical furnaces, and modern-day methods of mass-production have now been developed. Some other techniques such as acid-etching, sand-blasting, and mechanical pressing have progressed only in the last two hundred years.

5. **Melt-Quenching:** Melt-quenching is the easiest way for making up glass vessels. Small containers are shaped by straggling molten glass over on the end of a metal rod using a cooled clay core. As the final shape of the glass is formed, the rod is removed and the vessel is kept for annealing and the clay core scraped out.
6. **Casting:** The casting of glass involves the shaping of molten glass in a closed mold. Long ago this technique was used in the production of mosaic glass vessels. In this technique, thin slices of colored glass are fused. When mono color or colorless glass became popular during the Iron Age, an easier method was adopted for crafting open-shaped vessels. On the other hand, closed vessels were possibly cast through the lost-wax technique. In this method, a mold is made from wax or the object to be shaped is coated by the wax. Whereas, the model is covered using plaster or clay and baked thereafter. The wax melts leaving the mold into which molten or, the powdered glass could be poured. The vessels are allowed to cool after casting. After that, they are generally cut and ground into the final form.
7. **Blowing:** The glass-blowing was discovered slightly earlier than the middle of the first century BC. But the use of hollow metal blow-pipe came into practice approximately in the last quarter of the first century BC. The invention was widely accepted and much appreciated by the glassmakers. Such a fast technique of glass making changed the industry. It enabled glassmakers to make more vessels quickly and at a lower expense, with high flexibility of shapes.
8. **Mould-Blowing:** This method advanced from the development of the glass-blowing technique. It allows glassmakers to create copies of their designs at will. This technique used ready-made molds made up of clay, metal, or wood.
9. **Applications of Glass in Various Field:** Glass is a fully recyclable, pioneering material that has a lot of applications in every field. It is like an essential component of today's life. The uses of glass are mentioned in the following non-exhaustive list:
   - Packaging (food jars, drinking bottles, flacon for pharmaceuticals and cosmetics)
   - Tableware (glasses for drinking water, cup, plate, and bowl)
   - Housing and building material (windows, reinforcement structures, facades, conservatory)

- Furniture and Interior designing (face mirrors, partitions, glass tables, glass shelves, and lighting arrangements)
- Electronics and other Appliances (cooktops, TV, smart-phones, computer screens)
- Automotive and transport (windscreens, head or backlights, reinforced structural components, aircraft, ships, etc.)
- Made for protection from radiation such as X-Rays (radiology) and gamma-rays (nuclear)
- Optical fibers (Information technology)
- Renewable energy sources (solar-energy glass)

10. **Medical Uses of Smart Materials:** Shape memory polymers could be squeezed and inserted in the body and guided for a desirable action by providing proper stimulation. It can allow the creation of new antibiotics reacting in response to the change in body temperature. Nowadays, bio printing is also done using 3D printers with embedded smart materials.
11. **Improved Energy Devices:** The Possible use of shape memory alloys could be as sensors for detecting the position of the sun. In this way, solar panels could be set to auto-rotate facing towards the sunlight. In combination with recent controlled motors and motion controllers, The solar panels could be adjusted in the direction to obtain the maximum solar energy.
12. **Use of Smart Materials for Construction:** The Combination of traditional construction materials with smart materials could open immense possibilities in near future. The smart structures can be designed which indicate the damage or try to self-repair and adapt quickly to the ambiance. Some innovation-based companies such as DARPA's Engineered Living Materials (ELM) are looking forward to the use of living biomaterials for construction and architecture.
13. **Automotive and Aeronautics:** Airbus has started using some smart material responsive towards the temperature change to quickly cool down the jet engines and the wings are designed to decrease air resistance. Making devices adaptable to the surrounding conditions could be a chief advantage for a vast range of industries and is a prime goal of developing smart materials.

12.3 STRUCTURE

1. Categories of Smart Materials

i. Piezo-Electrics:

Piezo-electric materials transform electrical energy to mechanical distortion in itself or say mechanical energy and the reverse is also true. They deliver a vast variety

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of utility and can be utilized as actuators (generate a voltage in response to mechanical action), Many sensors, such as accelerometers can be designed. The voltage harvested because of the motion can be recorded and interpreted. One of the most common applications of a piezo-electric material is in lighters used in households to ignite the gas stove. In inkjet printer heads, such materials are used as actuators.

ii. Shape-Memory Alloys:

Nitinol is the most regularly presented Shape Memory Alloy (SMAs). This was natively developed at Naval Ordinance Laboratory. The phase of SMAs changes with the temperature, and they exert force or generate motion as a consequence. They move slowly but are proficient in fairly high energy. The materials demonstrating the shape memory effect include thermal switches, transforming structures, and some applications of applying high strain on the absorption of energy. Many advanced materials are still under development which includes magnetically activated SMAs.

iii. Magnetostrictive:

Analogous to the piezo-electric material that responds to change in electrical fields, these materials show responses towards the change in the magnetic field and as a result, it can behave as an actuator, or sensor if deformed. These materials show a large hysteresis which must be nullified while using them as sensors.

iv. Shape Memory Polymers (SMPs):

SMPs are analogous to SMAs (Shape Memory Alloys), however, they are constructed from a chained or cross-chained polymer network. SMPs have a high value of recoverable strain than the shape memory alloys, but generally under lower applied forces. Structural modifications for SMPs to fine-tune their properties is a huge area of research.

v. Hydrogels:

Hydrogels are useful because they can hold and absorb water or similarly other liquids, under certain ambient conditions. Hydrogels are of very good use on daily basis, especially used in disposable diapers. The main aspect of this material is that the gel can be chemically modified to react to different surrounding stimulations. New techniques have also been developed to turn these gels into a foam which allows systems to be constructed with the gels. Hydrogel-Activated Bulkhead Shaft Seals is one of its examples.

vi. Electro-Active Polymers:

Electro-active polymers exist in many forms and many others are still under investigation. Electro-active polymers are of great advantage as it is quite flexible to obtain superior property than the alloys or polymers discussed above in this

section. The targeted applications comprise sensing and energy harvesting. Moreover, the demand for high voltage, the low current actuator is also ongoing research in this field.

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vii. Bi-Component Fibers:

Smart clothing makes adaptive thermal insulation possible. In these materials, the thermal properties of the fabric change depending upon the ambient conditions. Recent research and developments have also developed such an advanced bi-component fiber technology where two different materials extrude simultaneously through a single orifice and they also change their shapes depending on the surrounding temperature.

12.4 PREPARATION METHODS

Various rapid cooling techniques such as spraying, spinning and laser deposition are used for the production of metallic glasses.

The melt spinning process technique involved in the preparation of metallic glass is illustrated in Figure 12.2.

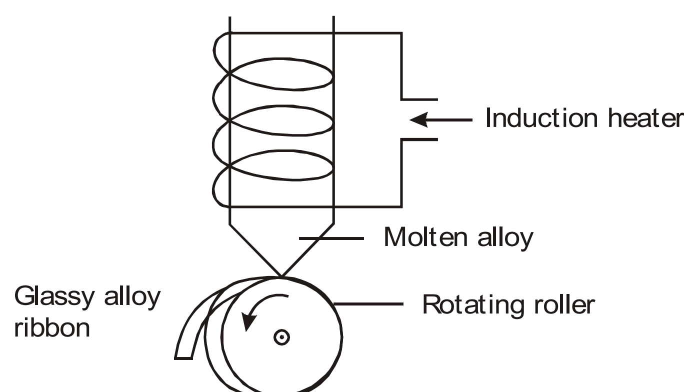


Fig. 12.2 *Melt Spinning Process Technique*

In this technique, there is a spinning disc made of copper. In order to prepare a metallic glass of a particular type, a suitable combination of metal-metal or metal-metalloid alloy in its stoichiometric ratio is taken in a refractory tube having a fine nozzle at its bottom. The nozzle side of the tube is placed just over the spinning disc.

An induction heater attached to the refractory tube melts the alloy. This melt is kept above its melting point till it gets transformed into a homogeneous mixture. An inert gas such as helium is made to flow through the tube containing the homogeneous mixture. As a result the melt gets ejected through the nozzle. The ejected melt is cooled at a faster rate with the help of the spinning cooled copper disc. The ejection rate can be increased by increasing the pressure of the inert gas. Thus, a glassy alloy ribbon starts getting formed over the spinning disc.

The thickness of the glassy ribbon may be varied by increasing or decreasing the speed of the spinning disc.

Other Techniques

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The other techniques used for producing ribbons of metallic glasses include:

(a) *Twin roller system* - In this technique a molten alloy is passed through two rollers rotating in opposite directions.

(b) *Melt extraction system* - In this technique a fast moving roller sweeps off molten droplet into a strip from a solid rod.

12.5 NOVEL PROPERTIES

1. The strength of metallic glasses is very high (nearly twice that of stainless steel) but they are lighter in weight.
2. They are ductile, malleable, brittle and opaque. The hardness is very high.
3. The toughness is very high, i.e., the fracture resistant is very high (more than ceramics).
4. They have high elasticity, i.e., the yield strength is high.
5. They have high corrosion resistance.
6. They do not contain any crystalline defects like point defects, dislocation, stacking faults, etc.
7. They are soft magnetic materials. As a result, easy magnetisation and demagnetisation are possible.
8. Magnetically soft metallic glasses have very narrow hysteresis loop, as shown in Figure 12.3. Thus, they have very low hysteresis energy losses.
9. They have high electrical resistivity which leads to a low eddy current loss.

The last two properties of metallic glasses makes it possible for them to be used as a transformer core.

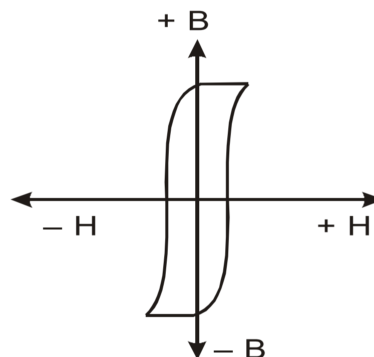


Fig. 12.3 *Hysteresis Loop of a Ferromagnetic Metallic Glass*

- Crystalline structure is not present.
- Sharp melting point does not exist.
- It Absorbs, transmits, or refracts light.
- Affected by alkalies.
- An exceptional electrical insulator even at high temperatures.
- It is enormously brittle.
- Available in many colors,
- Resistant towards air or water.
- Chemically very stable.
- Capable of being used in several ways.
- It is possible to join different pieces of glass through fusion.
- Because of the high developments in this field now it is even possible to form a glass softer than cotton, lighter than cork, or even stronger than steel.

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Check Your Progress

1. Give the definition of metallic glasses.
2. What is the piezo-electrics?
3. How is the electro-active polymers exist in many forms?
4. Explain about the other techniques used for production of metallic glasses.
5. Write the phenomenon of high resistivity in smart material.

12.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Most metals and alloys are crystalline, i.e., their atoms are arranged in a regular pattern that extends over a long distance. In contrast, a glass is an amorphous (non-crystalline), brittle and transparent solid.
2. Piezo-electric materials transform electrical energy to mechanical distortion in itself or say mechanical energy and the reverse is also true. They deliver a vast variety of utility and can be utilized as actuators (generate a voltage in response to mechanical action), Many sensors, such as accelerometers can be designed. The voltage harvested because of the motion can be recorded and interpreted.
3. Electro-active polymers exist in many forms and many others are still under investigation. Electro-active polymers are of great advantage as it is quite flexible to obtain superior property than the alloys or polymers discussed above in this section. The targeted applications comprise sensing and energy

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harvesting. Moreover, the demand for high voltage, the low current actuator is also ongoing research in this field.

4. The other techniques used for producing ribbons of metallic glasses include:
   (a) Twin roller system - In this technique a molten alloy is passed through two rollers rotating in opposite directions.
   (b) Melt extraction system - In this technique a fast moving roller sweeps off molten droplet into a strip from a solid rod.
5. They have high electrical resistivity which leads to a low eddy current loss. The last two properties of metallic glasses makes it possible for them to be used as a transformer core.

12.7 SUMMARY

- Most metals and alloys are crystalline, i.e., their atoms are arranged in a regular pattern that extends over a long distance. In contrast, a glass is an amorphous (non-crystalline), brittle and transparent solid.
- Metallic glasses are the metal alloys that are amorphous. That is, they do not have a long range atomic order. The major advantages of such glasses are that they are generally homogeneous in composition, and offer strong and superior corrosion resistance.
- One of the most common applications of a piezo-electric material is in lighters used in households to ignite the gas stove. In inkjet printer heads, such materials are used as actuators.
- Nitinol is the most regularly presented Shape Memory Alloy (SMAs). This was natively developed at Naval Ordinance Laboratory. The phase of SMAs changes with the temperature, and they exert force or generate motion as a consequence. They move slowly but are proficient in fairly high energy. Analogous to the piezo-electric material that responds to change in electrical fields, these materials show responses towards the change in the magnetic field and as a result, it can behave as an actuator, or sensor if deformed. These materials show a large hysteresis which must be nullified while using them as sensors.
- SMPs are analogous to SMAs (Shape Memory Alloys), however, they are constructed from a chained or cross-chained polymer network. SMPs have a high value of recoverable strain than the shape memory alloys, but generally under lower applied forces. Structural modifications for SMPs to fine-tune their properties is a huge area of research.
- Smart clothing makes adaptive thermal insulation possible. In these materials, the thermal properties of the fabric change depending upon the ambient conditions. Recent research and developments have also developed such

an advanced bi-component fiber technology where two different materials extrude simultaneously through a single orifice and they also change their shapes depending on the surrounding temperature.

- In this technique, there is a spinning disc made of copper. In order to prepare a metallic glass of a particular type, a suitable combination of metal-metal or metal-metalloid alloy in its stoichiometric ratio is taken in a refractory tube having a fine nozzle at its bottom. The nozzle side of the tube is placed just over the spinning disc.
- The other techniques used for producing ribbons of metallic glasses include:
  (a) Twin roller system - In this technique a molten alloy is passed through two rollers rotating in opposite directions.
  (b) Melt extraction system - In this technique a fast moving roller sweeps off molten droplet into a strip from a solid rod.
- They have high electrical resistivity which leads to a low eddy current loss. The last two properties of metallic glasses makes it possible for them to be used as a transformer core.

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12.8 KEY WORDS

- **Metallic glasses:** Metallic glasses are the newly developed engineering materials. Metallic glasses share the properties of both metals and alloys.
- **Amorphous materials:** Amorphous solids are well known by the definition that the atoms and molecules in an amorphous solid are not organized. Such materials are surrounding us in the form of plastic, gel, and glass.
- **Smart glasses:** Smart glasses can be defined by modifying the structure of the glass, or technologies that expand the performance of polymer- or glass-based products. These can be implemented through the surface coating, laminated structures with embedded electronic circuits.
- **Photo-optic glass:** Photo-optic glass is the one that changes color and the effect is stimulated by the photons.
- **Piezo-electric materials:** Piezo-electric materials transform electrical energy to mechanical distortion in itself or say mechanical energy and the reverse is also true. They deliver a vast variety of utility and can be utilized as actuators (generate a voltage in response to mechanical action).
- **Shape-Memory Alloys (SMAs):** Nitinol is the most regularly presented Shape Memory Alloy (SMAs). This was natively developed at Naval Ordinance Laboratory. The phase of SMAs changes with the temperature, and they exert force or generate motion as a consequence.
- **Magnetostrictive:** Analogous to the piezo-electric material that responds to change in electrical fields, these materials show responses towards the

change in the magnetic field and as a result, it can behave as an actuator, or sensor if deformed. These materials show a large hysteresis which must be nullified while using them as sensors.

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- **Hydrogels:** Hydrogels are useful because they can hold and absorb water or similarly other liquids, under certain ambient conditions.
- **Rapid cooling technique:** In this technique, there is a spinning disc made of copper. In order to prepare a metallic glass of a particular type, a suitable combination of metal-metal or metal-metalloid alloy in its stoichiometric ratio is taken in a refractory tube having a fine nozzle at its bottom. The nozzle side of the tube is placed just over the spinning disc.

12.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the amorphous materials.
2. Give the state phenomenon of glass transition.
3. What is the shape-memory alloys?
4. Explain about the rapid cooling technique.
5. Write the other techniques of production metallic glass.
6. Explain the novel properties of smart materials.

Long-Answer Questions

1. Explain briefly about the amorphous materials with its applications.
2. Briefly explain the structure and properties of glass material giving appropriate examples.
3. Discuss about the glass based type of functionality giving examples.
4. Explain the structure of smart materials giving appropriate examples.
5. Describe in detail the categories of smart materials giving appropriate examples.
6. Briefly explain the method of preparation for smart materials.
7. What are the novel properties of smart materials? Explain with the help of examples.

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UNIT 13 APPLICATIONS OF SMART MATERIALS

Structure

13.0 INTRODUCTION

Some metallic materials, return to their natural shape from the deformed state when heated. In a certain temperature range, the materials get strained to a certain level like 10 % but they regain their natural shape as soon as they are unloaded. Such an effect is known as thermal shape memory and super elasticity. Both of these effects depend upon the existence of a specific type of phase change called thermo elastic martensitic transformation. Such shape-related memories and super elastic alloys respond to the change in temperature and mechanical stresses in unconventional and astonishing ways. The material that has a shape memory can also be named 'Smart Materials'. In certain automotive, this effect of memorizing shapes is used to generate motion, force to form switches, and other smart tools. Moreover, super elasticity allows energy storage. Both of these effects have been worked upon by several scientists and engineers. However, only a few innovations have reached to marked and have touched an economic success. Recent applications have mainly come from the medical line. Such fields utilize the super elasticity and biocompatibility of Ni-Ti alloys. Smart materials were first reported in 1932 on gold-cadmium alloys. Along with this, later in the year 1938, the phase transformation was detected in the copper-zinc alloy (brass). Later in 1962, Beehler and his coworkers found the transformation in Nickel-Titanium and reported shape memory effect at the Naval Ordnance Laboratory and named these alloys as Nitinol after their laboratory.

Several years after the discovery of Nitinol, many other alloys were found with shape memory effect. Nevertheless, the development of products based upon smart materials began only after the discovery of Nitinol but it contains expansive

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materials. Only some alloy families based upon copper were found close to the properties attained for the Nitinol family as a commercially striking system. During the period of the 1980s and early 1990s, several manufacturers initiated to provide Ni-Ti materials and machineries, and a rising number of medical products were launched in the market. '*Shape memory alloys* are the alloys that could be distorted when they are cold but they return to their original or say remembered shape when heated. It seems that the alloys do have a memory. These are also known as memory alloys, memory metals, or smart metals. Shape Memory Alloys (SMAs) are known to demonstrate a structure-based reversible martensitic transition. At elevated temperatures, the SMAs exist as an austenite phase (described as memory phase) with long-range order.

Shape memory alloys exhibition super-elasticity that is a mechanical class of shape memory. This phenomenon is noticed when alloys are deformed just above the temperature of transformation. In the range of their different transformation temperature, the mechanical properties of SMAs also differ. Nickel titanium, also known as Nitinol, is a metal alloy of nickel and titanium, where the two elements are present in roughly equal atomic percentages. Different alloys are named according to the weight percentage of nickel, e.g. Nitinol 55 and Nitinol 60. It exhibits the shape memory effect and super elasticity at different temperatures.

In this unit, you will study about the shape of memory alloys, working mechanism of SMAs, pseudo elasticity, applications of SMAs, Nickel-Titanium (Nitinol) Alloy, material characteristic of Nitinol.

13.1 OBJECTIVES

After going through this unit, you will be able to:

- Define shape memory alloys
- Explain working mechanism of shape of memory alloy
- Elaborate of pseudo elasticity and its applications
- Provide important applications of shape memory alloys
- Illustrate the Nitinol and its structure
- Discuss about the characteristics of Nitinol and its mechanism

13.2 SHAPE MEMORY ALLOYS

Shape Memory Effect

As described in the above passage the "Shape Memory" defines the phenomenon of regaining the natural shape of a physically distorted body to its original shape by heating it. This effect occurs because of a crystalline phase-change termed

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as 'Thermo-Elastic Martensitic Transformation'. Shape memory alloys are martensitic, below the transition temperature. In such a situation, the microstructure is categorized by 'Self-Accommodating Twins'. The manensite is a soft material and it can be easily be deformed. Heating the material, above transformation temperature turns the material to its original shape and it also recovers its high strength (Refer Figure 13.1).

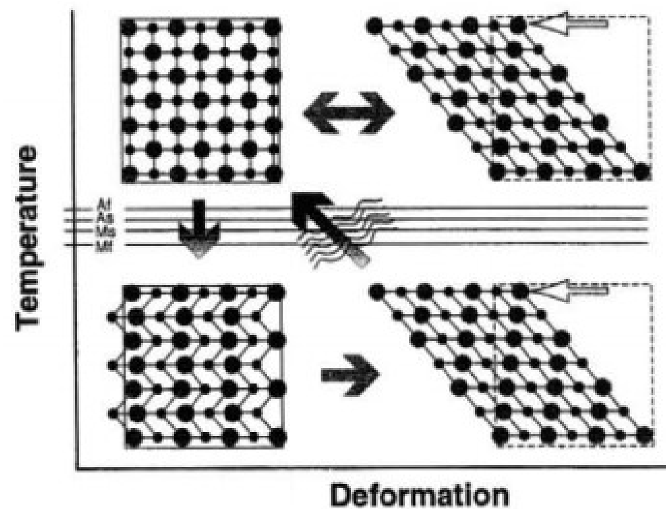


Fig. 13.1 *Schematic Demonstration of the Super-Elasticity and Shape Memory Effect*

Shape Memory Alloys

Shape memory alloys are the alloys that could be distorted when they are cold but they return to their original or say remembered shape when heated. It seems that the alloys do have a memory. These are also known as memory alloys, memory metals, or smart metals. Such alloys (Shape memory alloys - SMAs) exhibit two very exclusive properties, one of which is the pseudo-elasticity, and the other one is the shape memory effect. In 1938, Arne Olander was the one who observed these special properties, but until 1960, but no advance research was made in the field of shape memory alloys. Some of the most researched and extensively used alloys contain CuZnAl, NiTi (Nickel - Titanium), and CuAlNi.

Applications of Shape Memory Alloys

The scarce properties described in the last section are applicable to a vast variety of applications in several streams.

- **Bones**: Shape memory alloys can mend the broken bones.
- **Opening of Arteries and Veins:** In some cases, when the blood vessel has been clogged, an alloy tube is squeezed and inserted into the clogged vein and then allowed to expand.

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- **Dental Wires:** Such materials are used for making dental wires, and braces. Memory alloys maintain a stressed condition, on the teeth to shape them in a certain way.
- **Anti-Scalding Protection:** Memory metals are designed to restrict the flow of water by behaving differently at different temperatures. This helps to control the temperature in baths and showers.

Similarly, there could be many uses of these materials based on the above-mentioned properties such as switches, controllers, and somewhat temperature sensor-based applications.

13.3 WORKING MECHANISM

Working of Shape Memory Alloys

Shape Memory Alloys (SMAs) are known to demonstrate a structure-based reversible martensitic transition. At elevated temperatures, the SMAs exist as an austenite phase (described as memory phase) with long-range order. As the temperature reduces, the austenite phase transforms into a thermoelastic martensite phase. The thermoelastic martensite phase has several alternates, specially sheared platelets. Since the martensitic structure is self-compliant, its deformation on transformation to martensite does not exist. The martensite changing its shape through a twinning mechanism transforming different alternates to the shape that can accommodate the thoroughgoing elongation uni-directional with the direction of the applied force. The phase between platelets in the martensite structure slips very readily and the material is deformed at a comparatively lower value of applied stresses.

In contrast, there is only one possible orientation in austenite phase, therefore, all the possible deformed structures of the martensite phase return to the only possible orientation of the austenite phase (memorized phase), and ultimately the material recovers its shape we started with. Now, the temperature of transformation is dependent on the type of alloy. Besides its composition and other processing conditions such as applied thermomechanical treatments. The change in behavior while heating the alloy and cooling down the material does not match closely. Besides, such materials exhibit hysteresis. The extent of the hysteresis also changes with the type of alloy and in the range of 10 - 50 ^{o}C. A representative transformation curve is shown in the figure. In this case, the physical property of the alloy such as electrical resistance is shown to follow the phase transformations.

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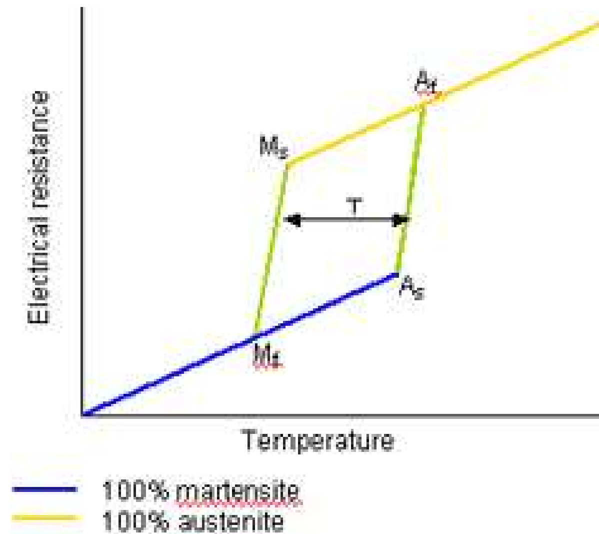


***Fig. 13.2** Thermal Transformation in SMAs*

Where Ms is the temperature at which martensite starts to form M_f. The temperature at which conversion to martensite is complete. 'As' is the temperature at which austenite starts to form 'A_f' is the temperature at which conversion to austenite. In this way, this is the Transformation of hysteresis as a whole.

13.4 PSEUDO ELASTICITY

Shape memory alloys exhibition super-elasticity that is a mechanical class of shape memory. This phenomenon is noticed when alloys are deformed just above the temperature of transformation. In the range of their different transformation temperature, the mechanical properties of SMAs also differ. The material exists in martensite phase and it could be torn or changed by a comparatively small applied force, at low temperature. Besides, on heating, it shows shape memory. Whereas, at high temperatures, the material shows an austenite phase, which can not be deformed easily. Also, no shape memory happens upon heating because there is no change in phase. Nevertheless, if this material is tested at a temperature just a little bit higher than its transformation temperature to austenite. In this scenario, the applied force transforms the austenite to martensite and the material shows an increase in the strain at fix applied force, and a significant change in shape happens for a comparatively smaller applied force. When the applied stress is detached, the martensite reverts to austenite and the original shape is recovered by the material. Such effect, in which the alloy seems extremely elastic, is recognized as super-elasticity or pseudoelasticity.

Applications of Shape Memory and Superelastic Alloys:

There are a number of patents exploiting the properties of shape memory alloys. However, a very small fraction of them has turned these properties into a successful

device. Undoubtfully, the applications are very wide in range from day-to-day user products to its medical achievements to its applications in space exploration. Only a small number of these applications can be described here. In 1969, the very first application happened when SMA-based joints were attached to the hydraulic pipes in the F-14 aircraft. This property has been stretched to connect different kinds of pipes. In some conditions, it uses a liner that is embraced onto a pipe to make a connection. Such connectors are cylindrical and these are cooled to an ultra-low temperature to make the martensitic phase when they can easily move over the pipes. Furthermore, on increasing the temperature above the transformation temperature, the joint returns back to its original shape and size but it is still constrained by the pipes. The couplings made by these alloys create enough stress to form a tight joint which sometimes is better than a normal welding process.

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Another application of these devices is to provide protection against fire. The water sprinkler can be smartly designed by the change in shape actuated by the heat generated in the fire. On the other hand, a safety valve containing SMA based controller can switch off the flow of a flammable liquid or gas in the case of a fire. Whereas, in the construction industry, an SMA-based clamp is used to hold the ceiling plates at their place if there is an increase in the temperature above 60 ^{o}C. This action protects pipes, cables, and the floor above from the fire.

Their shapes sensitive to temperature variation can be used as a modified bimetallic strip to regulate the temperature of the water. Similarly, an anti-scald device is attached to a shower to adding cold water to the pipeline if the temperature of the water turns out to be too high. This kind of device uses a spring of SMA and a compensatory spring made up of steel. As the temperature increases, the SMA-based spring expands and unlocks a needle valve leaving cold water to enter for mixing in with hot water. When the temperature decreases, the SMA returns to martensite phase and the spring made up of steel counters the effect and shuts the needle valve off.

A home appliance such as a deep fryer uses an SMA support which prevents the basket from being sunk into the oil until the optimum temperature of 170 ^{o}C is achieved. The applications to be used at high-temperature favor CuAlNi alloy. In this way, CuAlNi alloys are used in circuit breakers which is a kind of safety switch to save the circuit from an overload of electric current which as a consequence heats the wire. In case of the temperature of the heating wire reaches 140 ^{o}C, it cuts the lines off.

Superelastic alloys are used in making indestructible spectacle frames. Besides, superelastic wire is used to create some highly elastic springs. Super-elastic wires and tubes are used in many biomedical applications including catheters and the wires for guiding catheters. Super elastic arch-wires are used for orthodontic corrections.

In the future, the use of SMAs may become extremely important in terms of 'Smart Materials'. A variety of SMA shapes are crafted with reinforcement and kept as a backup system to protect the system in the worst-case scenario. In this

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way, smart materials use a higher volume of material and energy than is normally required. This is the only drawback of these materials. Smart materials can sense their local ambiance and can modify their behavior in extreme circumstances and provide extra security to the system. Smart materials are composites with sensors implanted. In a nutshell, sensors could be placed within a concrete structure, continuously checking for cracks or corrosion and the SMA actuators present in this would react to the strain caused by this degradation. The body of an aircraft would also contain a thin layer of sensors that would monitor even minor physical and chemical changes related to any minor to major damage and activate the SMAs to recompense for these changes and avoid failure.

Shape Memory Alloy Systems

In the year 1951, the shape memory effect was first recorded in AuCd alloy system. Since then Many other alloy systems have been developed. But it is worth mentioning that NiTi and some other copper-based alloys are useful for commercial application till today.

13.5 APPLICATIONS

Although a relatively wide variety of alloys are known to exhibit the SME, only some alloys find commercial applications. The most common SMA is an alloy of Nickel-Titanium (Ni - Ti). This alloy has been found to be the most useful of all SMAs. The generic name for the family of Ni–Ti alloy is Nitinol, which stands for Nickel Titanium Naval Ordnance Laboratory.

Other shape memory alloys include Cu – Al – Ni, Cu – Zn – Al and Co – Ni – Al. There is also a subfamily of SMAs known as Ferromagnetic Shape Memory Alloys (FSMAs) which are magnetically driven. The frequency of phase transformation is high in FSMAs compared to the cycles of heating and cooling. In this category only Ni – Mn – Ga ternary alloy has given satisfactory performance.

Other examples: Mn – Cu, Ti – Pd – Ni, Ni – Ti – Hf and In – Tl, etc.

Applications of SMAs

The crystal properties of SMA allow them to be applied in a number of different fields.

Aircraft and Space Industry

In this areas the SMAs can be used as fine-tuned helicopter blades and as lock ring electrical connectors. In addition, they are used in antenna opening, high-damping parts, hubble telescope and in triggering devices.

Automobile Industry

In this industry the SMAs are used in making spring actuators, clutch systems, thermostats, oil pressure control unit and high-pressure sealing plugs.

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Medical Field

The largest commercial application of SMAs is in the field of bioengineering and medical applications.

(a) They are used as dental arch wires. These wires make the misaligned teeth gradually return to their original shape exerting a small and nearly constant force on the misaligned teeth. The use of this wire causes less discomfort and is more efficient in faster tooth movement.

(b) They are also used as blood clot filter.

(c) Nitinol needle wire localizers are used to locate and mark breast tumours so that subsequent surgery can be more exact and less invasive.

(d) They are used to make tweezers to remove foreign objects through small incisions.

(e) They are used as guide wires for catheters through blood vessels.

(f) They are also used in designing micro-surgical instruments and micro-grippers, etc.

Consumer Products

(a) SMAs are used in making eye glass frames which offer improved comfort and flexibility and in cellular phone antenna.

(b) Nitinol is used in robotic actuators and micro-manipulators to stimulate human muscle motion.

(c) Ni-Ti springs in coffee pots can be trained to open a valve and release hot water at proper temperatures.

(d) Shape-memory-based toys and ornamental goods have been fabricated.

(e) SMAs can be used as couplers and fasteners.

(f) SMA-based fixed safety valves have been developed for industrial facilities.

(g) Temperature-sensitive SMA valves are used to instantly restrict water flow in shower or sinks.

(h) They can be used to design safety valves that provide emergency shutdown of process control lines that handle flammable and toxic fluid and gases.

Check Your Progress

1. Give the definition of shape memory alloy.
2. What is the applications of shape memory alloys?
3. Define the uses and drawback of smart materials.
4. Explain about the shape memory alloys exhibition super-elasticity.

13.6 NICKEL-TITANIUM (NITINOL) ALLOY

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Nickel-Titanium alloys are one of the famous SMAs used in many commercial applications. This structure is based upon the equiatomic construct of titanium and nickel atoms. It can bear fairly large numbers of shape memory strains. It is stable in structure, and resistant to corrosion as well. The temperature of transformation is very much dependent on the composition and even a minute change in the nickel content could cause ample change in the transformation temperature. This system also shows a huge transformation temperature hysteresis loop, of about 50 °C. A third metal is generally induced to such a binary alloy to modify its properties for commercial explorations. The shape memory effect almost remains the same if copper is added at the place of nickel up to 30%. Whereas it just reduces the width of the hysteresis to about 15 °C and it also makes it less sensitive towards the changes in the nickel content.

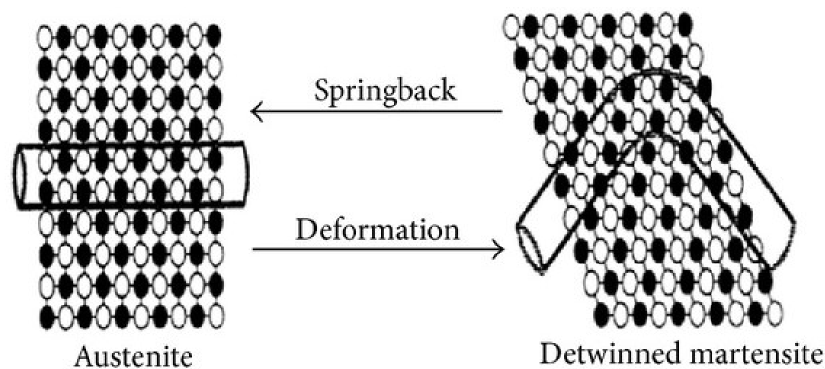


Fig. 13.3 *Diagrammatic Representation of the Superelasticity Effect of NiTi Alloy*

The addition of copper into the system is the most beneficial up to 10% of concentration. The addition of copper beyond this level only adds a small modification to the system. The manufacturing of NiTi alloys is not that easy just because the melting of all the components and the reaction of titanium must be performed in a vacuum or an inert atmosphere. That is also the reason because of which joining such alloys using welding, or soldering is the most difficult task. When it is done in a cold environment, the alloy becomes hard very quickly but it consists of a fine grain structure. In this case, very fine wires can be made easily. It is very hard to do machining with NiTi alloys. In this way, the alloy becomes very expensive to construct for a variety of applications. In spite of these drawbacks, its outstanding shape memory properties and resistance towards corrosion have given rise to NiTi being used in a vast variety of applications.

13.7 MATERIALS CHARACTERISTICS OF NITINOL

Nickel-Titanium, also known as **Nitinol**, is a metal alloy of nickel and titanium, where the two elements are present in roughly equal atomic percentages. Different

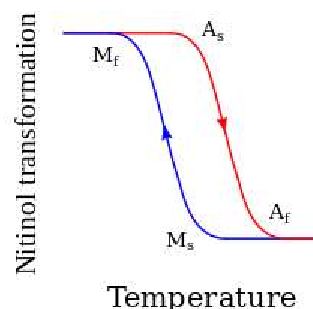
alloys are named according to the weight percentage of nickel, e.g. Nitinol 55 and Nitinol 60. It exhibits the shape memory effect and super elasticity at different temperatures.

Nitinol alloys exhibit two closely related and unique properties: the shape memory effect and super elasticity (also called pseudo elasticity). Shape memory is the ability of Nitinol to undergo deformation at one temperature, stay in its deformed shape when the external force is removed, then recover its original, undeformed shape upon heating above its 'Transformation Temperature'. Super elasticity is the ability for the metal to undergo large deformations and immediately return to its undeformed shape upon removal of the external load. Nitinol can deform 10-30 times as much as ordinary metals and return to its original shape. Whether Nitinol behaves with the shape memory effect or super elasticity depends on whether it is above the transformation temperature of the specific alloy. Below the transformation temperature it exhibits the shape memory effect, and above that temperature it behaves super elastically.

Mechanism

Nitinol's unusual properties are derived from a reversible solid-state phase transformation known as a martensitic transformation, between two different martensite crystal phases, requiring 10,000–20,000 psi (69–138 MPa) of mechanical stress.

At high temperatures, Nitinol assumes an interpenetrating simple cubic structure referred to as austenite (also known as the parent phase). At low temperatures, Nitinol spontaneously transforms to a more complicated monoclinic crystal structure known as martensite (daughter phase). There are four transition temperatures associated to the austenite-to-martensite and martensite-to-austenite transformations. Starting from full austenite, martensite begins to form as the alloy is cooled to the so-called martensite start temperature, or M_s, and the temperature at which the transformation is complete is called the martensite finish temperature, or M_f. When the alloy is fully martensite and is subjected to heating, austenite starts to form at the austenite start temperature, A_s, and finishes at the austenite finish temperature, A_f.



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Thermal Hysteresis of Nitinol's Phase Transformation

The cooling/heating cycle shows thermal hysteresis. The hysteresis width depends on the precise Nitinol composition and processing. Its typical value is a temperature range spanning about 20-50 K (20-50 °C; 36-90 °F) but it can be reduced or amplified by alloying and processing.

Crucial to Nitinol properties are two key aspects of this phase transformation. First is that the transformation is 'Reversible', meaning that heating above the transformation temperature will revert the crystal structure to the simpler austenite phase. The second key point is that the transformation in both directions is instantaneous.

Martensite's crystal structure (known as a monoclinic, or B19' structure) has the unique ability to undergo limited deformation in some ways without breaking atomic bonds. This type of deformation is known as twinning, which consists of the rearrangement of atomic planes without causing slip, or permanent deformation. It is able to undergo about 6–8% strain in this manner. When martensite is reverted to austenite by heating, the original austenitic structure is restored, regardless of whether the martensite phase was deformed. Thus the name 'Shape Memory' refers to the fact that the shape of the high temperature austenite phase is 'Remembered,' even though the alloy is severely deformed at a lower temperature.



Fig. 13.4 *2D View of Nitinol's Crystalline Structure during Cooling/Heating Cycle*

A great deal of pressure can be produced by preventing the reversion of deformed martensite to austenite — from 35,000 psi to, in many cases, more than 100,000 psi (689 MPa). One of the reasons that Nitinol works so hard to return to its original shape is that it is not just an ordinary metal alloy, but what is known as an intermetallic compound. In an ordinary alloy, the constituents are randomly positioned in the crystal lattice; in an ordered intermetallic compound, the atoms (in this case, nickel and titanium) have very specific locations in the lattice. The fact that Nitinol is an intermetallic is largely responsible for the complexity in fabricating devices made from the alloy.

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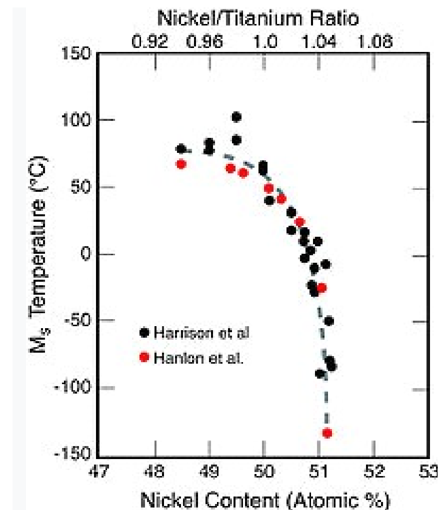


Fig. 13.5 *The Effect of Nitinol Composition on the Ms Temperature*

The scenario described above (cooling austenite to form martensite, deforming the martensite, then heating to revert to austenite, thus returning the original, undeformed shape) is known as the thermal shape memory effect. To fix the original 'Parent Shape,' the alloy must be held in position and heated to about 500 °C (932 °F). This process is usually called shape setting. A second effect, called superelasticity or pseudoelasticity, is also observed in Nitinol. This effect is the direct result of the fact that martensite can be formed by applying a stress as well as by cooling. Thus in a certain temperature range, one can apply a stress to austenite, causing martensite to form while at the same time changing shape. In this case, as soon as the stress is removed, the Nitinol will spontaneously return to its original shape. In this mode of use, Nitinol behaves like a super spring, possessing an elastic range 10–30 times greater than that of a normal spring material. There are, however, constraints: the effect is only observed about 273-313 K (0-40 °C; 32-104 °F) above the Af temperature. This upper limit is referred to as Md, which corresponds to the highest temperature in which it is still possible to stress-induce the formation of martensite. Below Md, martensite formation under load allows superelasticity due to twinning. Above Md, since martensite is no longer formed, the only response to stress is slip of the austenitic microstructure, and thus permanent deformation.

Nitinol is typically composed of approximately 50 to 51% nickel by atomic percent (55 to 56% weight percent). Making small changes in the composition can change the transition temperature of the alloy significantly. Transformation temperatures in Nitinol can be controlled to some extent, where Af temperature ranges from about "20 °C to +110 °C. Thus, it is common practice to refer to a Nitinol formulation as 'Superelastic' or 'Austenitic' if Af is lower than a reference temperature, while as 'Shape Memory' or 'Martensitic' if higher. The reference temperature is usually defined as the room temperature or the human body temperature (37 °C; 98 °F).

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One often-encountered effect regarding Nitinol is the so-called R-phase. The R-phase is another martensitic phase that competes with the martensite phase mentioned above. Because it does not offer the large memory effects of the martensite phase, it is usually of non-practical use.

Nitinol Technical Properties

Nitinol or Nickel Titanium (also known as NiTi) is in the unique class of shape memory alloys. Nitinol shape memory alloys can be modified to a great extent by changes in composition, mechanical working, and heat treatment.

Nitinol Transformation Properties

Transformation temperature		-200 to 110 deg. C
Latent heat of transformation		5.78 cal/g
Transformation strain (for polycrystalline material)	for a single cycle	max 8%
	for 100 cycles	6%
	for 100,000 cycles	4%
Hysteresis		30 to 50 deg. C

Nitinol Physical Properties

Melting point		1300 deg. C (2370 deg. F)
Density		6.45 g/cu.cm (0.233 lb/cu.in)
Thermal conductivity	austenite	0.18 W/cm * deg. C (10.4 BTU/ft * hr * deg. F)
	martensite	0.086 W/cm * deg. C (5.0 BTU/ft * hr * deg. F)
Coefficient of thermal expansion	austenite	11.0E-6/deg. C (6.11E-6/deg. F)
	martensite	6.6E-6/deg. C (3.67E-6/deg. F)
Specific heat		0.20 cal/g * deg. C (0.20 BTU/lb * deg. F)
Corrosion performance		excellent

Electrical and Magnetic Properties

Resistivity [resistance = resistivity * length / cross-sectional area]	austenite	approx. 100 micro-ohms * cm (39 micro-ohms * in)
	martensite	approx. 80 micro-ohms * cm (32 micro-ohms * in)
Magnetic permeability		< 1.002
Magnetic susceptibility		3.0E6 emu/g

Nitinol Mechanical Properties

Young's modulus****	austenite	approx. 83 GPa (12E6 psi)
	martensite	approx. 28 to 41 GPa (4E6 to 6E6 psi)
Yield strength	austenite	195 to 690 MPa (28 to 100 ksi)
	martensite	70 to 140 MPa (10 to 20 ksi)
Ultimate tensile strength	fully annealed	895 MPa (130 ksi)
	work hardened	1900 MPa (275 ksi)
	Poisson's ratio	0.33
Elongation at failure	fully annealed	25 to 50%
	work hardened	5 to 10%
Hot workability		quite good
Cold workability		difficult due to rapid work hardening
Machinability		difficult, abrasive techniques preferred

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Check Your Progress

5. Explain about the Nitinol alloy.
6. What is nickel titanium?
7. Define the technical properties of Nitinol.

13.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. 'Shape Memory' defines the phenomenon of regaining the natural shape of a physically distorted body to its original shape by heating it. This effect occurs because of a crystalline phase-change termed as "thermo-elastic martensitic transformation".
2. The scarce properties described in the last section are applicable to a vast variety of applications in several streams.
   - Bones: Shape memory alloys can mend the broken bones.
   - Opening of Arteries and Veins: In some cases, when the blood vessel has been clogged, an alloy tube is squeezed and inserted into the clogged vein and then allowed to expand.
   - Dental Wires: Such materials are used for making dental wires, and braces. Memory alloys maintain a stressed condition, on the teeth to shape them in a certain way.
   - Anti-Scalding Protection: Memory metals are designed to restrict the flow of water by behaving differently at different temperatures. This helps to control the temperature in baths and showers.

   Similarly, there could be many uses of these materials based on the above-mentioned properties such as switches, controllers, and somewhat temperature sensor-based applications.
3. Smart materials use a higher volume of material and energy than is normally required. This is the only drawback of these materials. Smart materials can sense their local ambiance and can modify their behaviour in extreme circumstances and provide extra security to the system. Smart materials are composites with sensors implanted.
4. Shape memory alloys exhibition super-elasticity that is a mechanical class of shape memory. This phenomenon is noticed when alloys are deformed just above the temperature of transformation. In the range of their different transformation temperature, the mechanical properties of SMAs also differ.
5. Nickel-Titanium alloys are one of the famous SMAs used in many commercial applications. This structure is based upon the equiatomic

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construct of titanium and nickel atoms. It can bear fairly large numbers of shape memory strains. It is stable in structure, and resistant to corrosion as well. The temperature of transformation is very much dependent on the composition and even a minute change in the nickel content could cause ample change in the transformation temperature.

6. Nickel titanium, also known as Nitinol, is a metal alloy of nickel and titanium, where the two elements are present in roughly equal atomic percentages. Different alloys are named according to the weight percentage of nickel, for example Nitinol 55 and Nitinol 60. It exhibits the shape memory effect and super elasticity at different temperatures. Nitinol alloys exhibit two closely related and unique properties: the shape memory effect and super elasticity (also called pseudo elasticity).
7. The technical properties of Nitinol can be defined as, Nitinol or Nickel Titanium (also known as NiTi) is in the unique class of shape memory alloys. Nitinol shape memory alloys can be modified to a great extent by changes in composition, mechanical working, and heat treatment.

13.9 SUMMARY

- 'Shape Memory' defines the phenomenon of regaining the natural shape of a physically distorted body to its original shape by heating it. This effect occurs because of a crystalline phase-change termed as 'Thermo-Elastic Martensitic Transformation'.
- Shape memory alloys are the alloys that could be distorted when they are cold but they return to their original or say remembered shape when heated. It seems that the alloys do have a memory. These are also known as memory alloys, memory metals, or smart metals.
- Dental wires: Such materials are used for making dental wires, and braces. Memory alloys maintain a stressed condition, on the teeth to shape them in a certain way.
- Shape Memory Alloys (SMAs) are known to demonstrate a structure-based reversible martensitic transition. At elevated temperatures, the SMAs exist as an austenite phase (described as memory phase) with long-range order.
- The extent of the hysteresis also changes with the type of alloy and in the range of 10 - 50 ^{o}C. A representative transformation curve is shown in the figure. In this case, the physical property of the alloy such as electrical resistance is shown to follow the phase transformations.
- Shape memory alloys exhibition super-elasticity that is a mechanical class of shape memory. This phenomenon is noticed when alloys are deformed just above the temperature of transformation. In the range of their

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different transformation temperature, the mechanical properties of SMAs also differ.

- At high temperatures, the material shows an austenite phase, which can not be deformed easily. Also, no shape memory happens upon heating because there is no change in phase. Nevertheless, if this material is tested at a temperature just a little bit higher than its transformation temperature to austenite.
- The properties of shape memory alloys. However, a very small fraction of them has turned these properties into a successful device. Undoubtfully, the applications are very wide in range from day-to-day user products to its medical achievements to its applications in space exploration.
- The water sprinkler can be smartly designed by the change in shape actuated by the heat generated in the fire. On the other hand, a safety valve containing SMA based controller can switch off the flow of a flammable liquid or gas in the case of a fire.
- Shapes sensitive to temperature variation can be used as a modified bimetallic strip to regulate the temperature of the water. Similarly, an anti-scald device is attached to a shower to adding cold water to the pipeline if the temperature of the water turns out to be too high.
- Superelastic alloys are used in making indestructible spectacle frames. Besides, superelastic wire is used to create some highly elastic springs. Super-elastic wires and tubes are used in many biomedical applications including catheters and the wires for guiding catheters. Super elastic arch-wires are used for orthodontic corrections.
- In the year 1951, the shape memory effect was first recorded in AuCd alloy system. Since then Many other alloy systems have been developed. But it is worth mentioning that NiTi and some other copper-based alloys are useful for commercial application till today.
- Although a relatively wide variety of alloys are known to exhibit the SME, only some alloys find commercial applications. The most common SMA is an alloy of nickel titanium (Ni – Ti). This alloy has been found to be the most useful of all SMAs. The generic name for the family of Ni–Ti alloy is Nitinol, which stands for Nickel Titanium Naval Ordnance Laboratory.
- In this areas the SMAs can be used as fine-tuned helicopter blades and as lock ring electrical connectors. In addition, they are used in antenna opening, high-damping parts, hubble telescope and in triggering devices.
- Nitinol needle wire localizers are used to locate and mark breast tumours so that subsequent surgery can be more exact and less invasive.
- Nickel-Titanium alloys are one of the famous SMAs used in many commercial applications. This structure is based upon the equiatomic construct of titanium and nickel atoms. It can bear fairly large numbers of

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shape memory strains. It is stable in structure, and resistant to corrosion as well. The temperature of transformation is very much dependent on the composition and even a minute change in the nickel content could cause ample change in the transformation temperature.

- The shape memory effect almost remains the same if copper is added at the place of nickel up to 30%. Whereas it just reduces the width of the hysteresis to about 15 ^{o}C and it also makes it less sensitive towards the changes in the nickel content.

13.10 KEY WORDS

- **Shape memory alloy:** "Shape Memory" defines the phenomenon of regaining the natural shape of a physically distorted body to its original shape by heating it. This effect occurs because of a crystalline phase-change termed as "thermo-elastic martensitic transformation".
- **Superelastic alloys:** Superelastic alloys are used in making indestructible spectacle frames. Besides, superelastic wire is used to create some highly elastic springs. Super-elastic wires and tubes are used in many biomedical applications including catheters and the wires for guiding catheters. Super elastic arch-wires are used for orthodontic corrections.
- **Shape memory alloy systems:** In the year 1951, the shape memory effect was first recorded in AuCd alloy system. Since then Many other alloy systems have been developed. But it is worth mentioning that NiTi and some other copper-based alloys are useful for commercial application till today.
- **Nickel-Titanium alloys:** Nickel-Titanium alloys are one of the famous SMAs used in many commercial applications. This structure is based upon the equiatomic construct of titanium and nickel atoms. It can bear fairly large numbers of shape memory strains. It is stable in structure, and resistant to corrosion as well.
- **Nitinol:** Nickel Titanium, also known as Nitinol, is a metal alloy of Nickel and Titanium, where the two elements are present in roughly equal atomic percentages. Different alloys are named according to the weight percentage of nickel.

13.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the term shape memory effect.
2. What is shape memory alloy?

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3. Explain the term super-elasticity.
4. Give the applications of SMAs in medical field.
5. Draw the structure of Nitinol alloy.
6. Explain the importance of Nickel Titanium.
7. What is martensite start temperature?

Long-Answer Questions

1. Explain briefly about the shape memory alloy and its applications giving examples.
2. Elaborate on the working mechanism of SMAs with the help of examples.
3. Discuss about the pseudo elasticity giving its properties and applications.
4. Briefly explain about the applications of SMAs in various fields.
5. Discuss in detail about Nitinol and its structure with the help of appropriate examples.
6. Explain about the working mechanism of Nitinol giving examples.
7. Discuss in detail about the material characteristics of Nitinol.

13.12 FURTHER READINGS

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UNIT 14 MICRO ELECTRO MECHANICAL SYSTEM

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Structure

14.0 INTRODUCTION

Micro Electro Mechanical Systems (MEMS), also written as micro-electro-mechanical systems (or microelectronic and microelectromechanical systems) and the related micro mechatronics and microsystems constitute the technology of microscopic devices, particularly those with moving parts. They merge at the nanoscale into Nano Electro Mechanical Systems (NEMS) and nanotechnology. MEMS are also referred to as micro machines in Japan and Micro System Technology (MST) in Europe. MEMS are made up of components between 1 and 100 micrometres in size (i.e., 0.001 to 0.1 mm), and MEMS devices generally range in size from 20 micrometres to a millimetre (i.e., 0.02 to 1.0 mm), although components arranged in arrays (e.g., digital micro mirror devices) can be more than 1000 mm^2. They usually consist of a central unit that processes data (an integrated circuit chip, such as microprocessor) and several components that interact with the surroundings (such as, micro sensors). Because of the large surface area to volume ratio of MEMS, forces produced by ambient electromagnetism (e.g., electrostatic charges and magnetic moments), and fluid dynamics (e.g., surface tension and viscosity) are more important design considerations than with larger scale mechanical devices. MEMS technology is distinguished from molecular nanotechnology or molecular electronics in that the latter must also consider surface chemistry.

Silicon is the material used to create most integrated circuits used in consumer electronics in the modern industry. The economies of scale, ready availability of inexpensive high-quality materials, and ability to incorporate electronic functionality make silicon attractive for a wide variety of MEMS applications. By means of electrochemical treatment, crystalline silicon can be permeated with tiny,

nanostructured pores that entirely change the characteristics and properties of the material. One prominent example of this can be seen in the interaction of porous silicon with living cells, which can be totally unwilling to settle on smooth silicon surfaces but readily adhere to porous silicon, giving rise to great hopes.

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The piezo-resistive effect is a change in the electrical resistivity of a semiconductor or metal when mechanical strain is applied. In contrast to the piezoelectric effect, the piezo-resistive effect causes a change only in electrical resistance, not in electric potential.

In this unit, you will study about the introduction to Micro Electro Mechanical Systems (MEMS), silicon, porous silicon and silicon oxide based MEMS, fabrication of piezoelectric and piezo-resistive MEMS materials, application to micro-actuators and micro-accelerometers.

14.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the significance of Micro Electro Mechanical System (MEMS)
- Define about the silicon, porous silicon and silicon oxide based MEMS
- Analyse the fabrication of piezoelectric and piezo-resistive MEMS material
- Elaborate on the important applications of micro-actuators and micro-accelerometers

14.2 INTRODUCTION TO MICRO ELECTRO MECHANICAL SYSTEM (MEMS)

Micro Electro Mechanical Systems (MEMS), also written as micro-electro-mechanical systems (or microelectronic and microelectromechanical systems) and the related micro mechatronics and microsystems constitute the technology of microscopic devices, particularly those with moving parts. They merge at the nanoscale into Nano Electro Mechanical Systems (NEMS) and nanotechnology. MEMS are also referred to as micro machines in Japan and Micro System Technology (MST) in Europe. MEMS are made up of components between 1 and 100 micrometres in size (i.e., 0.001 to 0.1 mm), and MEMS devices generally range in size from 20 micrometres to a millimetre (i.e., 0.02 to 1.0 mm), although components arranged in arrays (e.g., digital micro mirror devices) can be more than 1000 mm2. They usually consist of a central unit that processes data (an integrated circuit chip, such as microprocessor) and several components that interact with the surroundings (such as, micro sensors). Because of the large surface area to volume ratio of MEMS, forces produced by ambient electromagnetism (e.g., electrostatic charges and magnetic moments), and fluid dynamics (e.g., surface tension and viscosity) are more important design considerations than with larger

scale mechanical devices. MEMS technology is distinguished from molecular nanotechnology or molecular electronics in that the latter must also consider surface chemistry.

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The potential of very small machines was appreciated before the technology existed that could make them. MEMS became practical once they could be fabricated using modified semiconductor device fabrication technologies, normally used to make electronics. These include molding and plating, wet etching [KOH (Potassium Hydroxide) and TMAH (Tetramethylammonium Hydroxide)] and dry etching [RIE (Reactive-Ion Etching) and DRIE (Deep Reactive-Ion Etching)], Electrical Discharge Machining (EDM), and other technologies capable of manufacturing small devices.

Types of MEMS

There are two basic types of MEMS switch technology: capacitive and ohmic. A capacitive MEMS switch is developed using a moving plate or sensing element, which changes the capacitance. Ohmic switches are controlled by electrostatically controlled cantilevers. Ohmic MEMS switches can fail from metal fatigue of the MEMS actuator (cantilever) and contact wear, since cantilevers can deform over.

Materials for MEMS Manufacturing

The fabrication of MEMS evolved from the process technology in semiconductor device fabrication, i.e., the basic techniques are deposition of material layers, patterning by photolithography and etching to produce the required shapes.

Silicon

Silicon is the material used to create most integrated circuits used in consumer electronics in the modern industry. The economies of scale, ready availability of inexpensive high-quality materials, and ability to incorporate electronic functionality make silicon attractive for a wide variety of MEMS applications. Silicon also has significant advantages engendered through its material properties. In single crystal form, silicon is an almost perfect Hookean material, meaning that when it is flexed there is virtually no hysteresis and hence almost no energy dissipation. As well as making for highly repeatable motion, this also makes silicon very reliable as it suffers very little fatigue and can have service lifetimes in the range of billions to trillions of cycles without breaking. Semiconductor nanostructures based on silicon are gaining increasing importance in the field of microelectronics and MEMS in particular. Silicon nanowires, fabricated through the thermal oxidation of silicon, are of further interest in electrochemical conversion and storage, including nanowire batteries and photovoltaic systems.

Polymers

Even though the electronics industry provides an economy of scale for the silicon industry, crystalline silicon is still a complex and relatively expensive material to

produce. Polymers on the other hand can be produced in huge volumes, with a great variety of material characteristics. MEMS devices can be made from polymers by processes, such as injection molding, embossing or stereo lithography and are especially well suited to microfluidic applications such as disposable blood testing cartridges.

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Metals

Metals can also be used to create MEMS elements. While metals do not have some of the advantages displayed by silicon in terms of mechanical properties, when used within their limitations, metals can exhibit very high degrees of reliability. Metals can be deposited by electroplating, evaporation, and sputtering processes. Commonly used metals include gold, nickel, aluminium, copper, chromium, titanium, tungsten, platinum, and silver.

Ceramics

The nitrides of silicon, aluminium and titanium as well as silicon carbide and other ceramics are increasingly applied in MEMS fabrication due to advantageous combinations of material properties. AlN crystallizes in the wurtzite structure and thus shows pyroelectric and piezoelectric properties enabling sensors, for instance, with sensitivity to normal and shear forces. TiN, on the other hand, exhibits a high electrical conductivity and large elastic modulus, making it possible to implement electrostatic MEMS actuation schemes with ultrathin beams. Moreover, the high resistance of TiN against bio corrosion qualifies the material for applications in biogenic environments. The figure shows an electron-microscopic picture of a MEMS biosensor with a 50 nm thin bendable TiN beam above a TiN ground plate. Both can be driven as opposite electrodes of a capacitor, since the beam is fixed in electrically isolating side walls. When a fluid is suspended in the cavity its viscosity may be derived from bending the beam by electrical attraction to the ground plate and measuring the bending velocity.

14.3 SILICON, POROUS SILICON AND SILICON OXIDE BASED MEMS

Silicon

Silicon is the material used to create most integrated circuits used in consumer electronics in the modern industry. The economies of scale, ready availability of inexpensive high-quality materials, and ability to incorporate electronic functionality make silicon attractive for a wide variety of MEMS applications. Silicon also has significant advantages engendered through its material properties. In single crystal form, silicon is an almost perfect Hookean material, meaning that when it is flexed there is virtually no hysteresis and hence almost no energy dissipation. As well as making for highly repeatable motion, this also makes silicon very reliable as it

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Porous Silicon

Porous silicon (abbreviated as 'PS' or 'pSi') is a form of the chemical element silicon that has introduced Nano pores in its microstructure, rendering a large surface to volume ratio in the order of 500 m^2/cm^3.

Porous silicon was discovered by accident in 1956 by Arthur Uhlir Jr. and Ingeborg Uhlir at the Bell Labs in the U.S. At the time, the Ulhirs were in the process of developing a technique for polishing and shaping the surfaces of silicon and germanium. However, it was found that under several conditions a crude product in the form of thick black, red or brown film were formed on the surface of the material. At the time, the findings were not taken further and were only mentioned in Bell Lab's technical notes. Despite the discovery of porous silicon in the 1950s, the scientific community was not interested in porous silicon until the late 1980s. At the time, Leigh Canham – while working at the Defence Research Agency in England – reasoned that the porous silicon may display quantum confinement effects. The intuition was followed by successful experimental results published in 1990. In the published experiment, it was revealed that silicon wafers can emit light if subjected to electrochemical and chemical dissolution.

Anodization and stain-etching are the two most common methods used for fabrication of porous silicon, however, there are almost twenty other methods to fabricate this material. Drying and surface modification might be needed afterwards. If anodization in an aqueous solution is used to form microporous silicon, the material is commonly treated in ethanol immediately after fabrication, to avoid damage to the structure that results due to the stresses of the capillary effect of the aqueous solution.

Silicon Oxide

Silicon is considered as the most significant material for almost all of the MEMS devices. This is mainly because of the economic benefits owing to the firm semiconductor manufacturing technology which provides the industrial infrastructure essential for the MEMS fabrication. These are the additional and necessary properties of silicon including electrical, optical and mechanical which is linked to different crystal structures. Subsequently, due to the well-established and firm techniques of micromachining along with the additive and subtractive processes makes the design and mass production of Si-MEMS simple, easy and economical. Si-based MEMS may include some other materials whose properties are compatible with the silicon. These materials include silicon oxides, silicon nitrides,

silicon carbides and metals, such as Al (Aluminium), W (Tungsten), Cu (Copper) and polymers, such as polyimide.

Hydrofluoric acid is commonly used as an aqueous etchant for silicon dioxide (SiO_2, also known as BOX for SOI), usually in 49% concentrated form, 5:1, 10:1 or 20:1 BOE (Buffered Oxide Etchant) or BHF (Buffered HF). They were first used in medieval times for glass etching. It was used in IC fabrication for patterning the gate oxide until the process step was replaced by RIE.

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Hydrofluoric acid is considered one of the more dangerous acids in the cleanroom. It penetrates the skin upon contact and it diffuses straight to the bone. Therefore, the damage is not felt until it is too late

14.4 FABRICATION OF PIEZO-ELECTRIC AND PIEZO-RESISTIVE MEMS MATERIAL

Fabrication of Piezo-Electric Materials

A piezoelectric Micro Electro Mechanical System (piezo MEMS) is a miniature or microscopic device that uses piezoelectricity to generate motion and carry out its tasks. It is a micro electro mechanical system that takes advantage of an electrical potential that appears under mechanical stress. Piezo MEMS can be found in a variety of applications, such as switches, inkjet printer heads, sensors, micro pumps, and energy harvesters.

Piezo MEMS technology began around the early 1990s as scientist's explored alternatives to electrostatic actuation in Radio Frequency (RF) Micro Electro Mechanical Systems (MEMS). For RF MEMS, electrostatic actuation specialized high voltage charge pump circuits due to small electrode gap spacing and large driving voltages. In contrast, piezoelectric actuation allowed for high sensitivity as well as low voltage and power consumption as low as a few millivolts. It also had the ability to close large vertical gaps while still allowing for low microsecond operating speeds. Lead Zirconate Titanate (PZT), in particular, offered the most promise as a piezoelectric material because of its high piezoelectric coefficient, tunable dielectric constant, and electromechanical coupling coefficient. Piezo MEMS have been applied to various different technologies from switches to sensors, and further research have led to the creation of piezoelectric thin films, which aided in the realization of highly integrated piezo MEMS devices

Design

There exists three primary approaches to realizing Piezo MEMS devices:

1. **The Additive Approach**: The piezoelectric thin films are deposited on silicon substrates with layers of insulating and conducting material followed by surface or silicon bulk micromachining.

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2. **The Subtractive Approach**: Single crystal or polycrystalline piezo electrics and piezo ceramics are subjected to direct bulk micromachining and then electrode.
3. **The Integrative Approach:** Micro machined structures are integrated in silicon or piezo electrics by using bonding techniques on bulk piezoelectric or silicon substrates.

Piezo MEMS use two principal crystal structures, the wurtzite and perovskite structures.

Piezo MEMS still face many difficulties that impede its ability to be successfully commercialized. For instance, the success of depositing uniform films of piezo electrics still depend heavily on the use of appropriate layers of proper nucleation and film growth. As a result, extensive device-specific development efforts are needed to create a proper sensor structure. In addition, researchers continue to search for ways to reduce and control the material and sensor drift and aging characteristics of thin film piezoelectric materials. Deposition techniques to create thin films with properties approaching those of bulk materials remain in development and in need of improvement. Furthermore, the chemistry and etching characteristics of most piezoelectric materials remain very slow.

Fabrication Piezo-Resistive MEMS Materials

The piezo-resistive effect is a change in the electrical resistivity of a semiconductor or metal when mechanical strain is applied. In contrast to the piezoelectric effect, the piezo-resistive effect causes a change only in electrical resistance, not in electric potential. The change of electrical resistance in metal devices due to an applied mechanical load was first discovered in 1856 by Lord Kelvin. With single crystal silicon becoming the material of choice for the design of analogy and digital circuits, the large piezo-resistive effect in silicon and germanium was first discovered in 1954 (Smith 1954).

Mechanism

In conducting and semi-conducting materials, changes in inter-atomic spacing resulting from strain affect the bandgaps, making it easier (or harder depending on the material and strain) for electrons to be raised into the conduction band. This results in a change in resistivity of the material. Within a certain range of strain this relationship is linear, so that the piezo-resistive coefficient. . Usually the resistance change in metals is mostly due to the change of geometry resulting from applied mechanical stress. However, even though the piezo-resistive effect is small in those cases it is often not negligible. In cases where it is, it can be calculated using the simple resistance equation derived from Ohm’s law.

Piezo-Resistors

Piezo-resistors are resistors made from a piezo-resistive material and are usually used for measurement of mechanical stress. They are the simplest form of piezo-resistive devices.

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Fabrication

Piezo-resistors can be fabricated using wide variety of piezo-resistive materials. The simplest form of piezo-resistive silicon sensors are diffused resistors. Piezo-resistors consist of a simple two contact diffused n- or p-wells within a p- or n-substrate. As the typical square resistances of these devices are in the range of several hundred ohms, additional p^+ or n^+ plus diffusions are a potential method to facilitate ohmic contacts to the device.

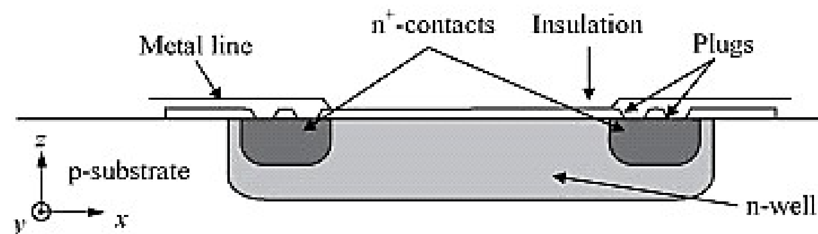


Fig. 14.1 *Schematic Cross-Section of the Basic Elements of a Silicon n-Well Piezo-Resistor*

14.5 APPLICATION TO MICRO-ACTUATORS AND MICRO-ACCELEROMETERS

Applications to Micro-Actuators

Micro actuators are small-scale active devices capable of generating mechanical motion of solids or fluids. Motion is generated via converting one form of energy (for instance electrical) into kinetic energy. Typical sizes of micro actuators vary from a few millimetres to a few micrometres, but total sizes can reach centimetres when packaged. When generating mechanical motion of solids, typical displacements are in the nanometre to millimetre range, and typical forces generated are in the Nano Newton to mili Newton range. For microfluidic actuators, typical flow rates generated are in the pico Liter/minute to microliter/minute ranges.

There potential applications of micro actuators are widespread and include inertial sensors, optical MEMS and lab-on-a-chip, manipulators, micro robots, and micro surgery. Each domain has its typical requirements in terms of forces, displacements, materials, frequencies, voltage vs. current control, etc.

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Micro actuators have proved themselves to be the key elements for almost all kinds of microsystems. Hardly found as stand-alone components, they are typically integrated into systems. The most obvious example, and simultaneously the most popular device, is the electrostatic comb actuator, which is found as an integrated part of in numerous inertial sensors. Its exclusive achievement is due to its simple and scalable design, and its dependable integrated manufacturing process via the ICP. In addition, magnetic, piezo electric, shape memory, pneumatic, and hydraulic principles have been explored for micro actuation, each of which have its own limits of integration, process complexity, and applicability. Also, over the past few years, living cells, such as cardio myocytes, muscle cells, and whole dorsal vessels, have been combined with technical systems and have resulted in new types of bio micro actuators. However, most of them challengingly require an aqueous environment and only have a limited lifetime. Introducing smart materials in micro systems skills, novel smart micro actuators and sensors are currently being developed, e.g., for mobile, wearable, and implantable MEMS (Micro-Electro-Mechanical-System) devices. Magnetic Shape Memory Alloys (MSMAs) are a promising material system as they show multiple coupler belongings as well as large, unexpected changes in their physical properties, e.g., of strain and magnetization, due to a first order phase transformation. For the development of MSMA micro actuators, considerable efforts are undertaken to fabricate MSMA foils and films showing similar and just as strong effects compared to their bulk counterparts. Novel MEMS-compatible technologies are being developed to enable their micromachining and integration. This review gives an overview of material properties, engineering issues and fabrication technologies. Selected demonstrators are presented illustrating the wide application potential.

Applications to Micro-Accelerometers

An accelerometer is a tool that measures proper acceleration. Proper acceleration is the acceleration (the rate of change of velocity) of a body in its own instantaneous rest frame, this is different from coordinate acceleration, which is acceleration in a fixed coordinate system. For example, an accelerometer at rest on the surface of the Earth will measure an acceleration due to Earth's gravity, straight upwards, Accelerometers have many uses in industry and science. Highly sensitive accelerometers are used in inertial navigation systems for aircraft and missiles. Vibration in rotating machines is monitored by accelerometers. They are used in tablet computers and digital cameras so that images on screens are always displayed upright. In unmanned aerial vehicles, accelerometers help to stabilise flight. When two or more accelerometers are coordinated with one another, they can measure differences in proper acceleration, particularly gravity, over their separation in space—that is, the gradient of the gravitational field. Gravity gradiometer is useful because absolute gravity is a weak effect and depends on the local density of the Earth, which is quite variable.

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Single- and multi-axis accelerometers can detect both the magnitude and the direction of the proper acceleration, as a vector quantity, and can be used to sense orientation (because the direction of weight changes), coordinate acceleration, vibration, shock, and falling in a resistive medium (a case in which the proper acceleration changes, increasing from zero). Micro machined Micro Electro Mechanical Systems (MEMS) accelerometers are increasingly present in portable electronic devices and video-game controllers, to detect changes in the positions of these devices.

Applications

Engineering: Accelerometers can be used to measure vehicle acceleration. Accelerometers can be used to measure vibration on cars, machines, buildings, process control systems and safety installations. They can also be used to measure seismic activity, inclination, machine vibration, dynamic distance and speed with or without the influence of gravity. Applications for accelerometers that measure gravity, wherein an accelerometer is specifically configured for use in gravimeter, are called gravimeters.

Notebook computers equipped with accelerometers can contribute to the Quake-Catcher Network (QCN), a BOINC project aimed at scientific research of earthquakes

Biology: Accelerometers are also increasingly used in the biological sciences. High frequency recordings of bi-axial or tri-axial acceleration allows the discrimination of behavioural patterns while animals are out of sight. Furthermore, recordings of acceleration allow researchers to quantify the rate at which an animal is expending energy in the wild, by either determination of limb-stroke frequency or measures such as overall dynamic body acceleration Such approaches have mostly been adopted by marine scientists due to an inability to study animals in the wild using visual observations, however an increasing number of terrestrial biologists are adopting similar approaches. For example, accelerometers have been used to study flight energy expenditure of Harris's Hawk (Parabuteo unicinctus) . Researchers are also using smartphone accelerometers to collect and extract mechano-biological descriptors of resistance exercise.

Industry: Accelerometers are also used for machinery health monitoring to report the vibration and its changes in time of shafts at the bearings of rotating equipment such as turbines, pumps, fans, rollers, compressors, or bearing fault which, if not attended to promptly, can lead to costly repairs. Accelerometer vibration data allows the user to monitor machines and detect these faults before the rotating equipment fails completely.

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Check Your Progress

1. Define the term MEMS.
2. Explain about the silicon based MEMS.
3. Elaborate on the piezo electric MEMS material.
4. What do you understand by the piezo-resistive MEMS material?
5. What is micro-accelerometers?

14.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. MEMS are made up of components between 1 and 100 micrometres in size (i.e., 0.001 to 0.1 mm), and MEMS devices generally range in size from 20 micrometres to a millimetre (i.e., 0.02 to 1.0 mm), although components arranged in arrays (e.g., digital micro mirror devices) can be more than 1000 mm^2. They usually consist of a central unit that processes data (an integrated circuit chip, such as microprocessor) and several components that interact with the surroundings (such as, micro sensors).
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3. A piezoelectric Micro Electro Mechanical System (piezo MEMS) is a miniature or microscopic device that uses piezoelectricity to generate motion and carry out its tasks. It is a micro electro mechanical system that takes advantage of an electrical potential that appears under mechanical stress. Piezo MEMS can be found in a variety of applications, such as switches, inkjet printer heads, sensors, micro pumps, and energy harvesters.
4. The piezo-resistive effect is a change in the electrical resistivity of a semiconductor or metal when mechanical strain is applied. In contrast to the piezoelectric effect, the piezo-resistive effect causes a change only in electrical resistance, not in electric potential.
5. Micro actuators are small-scale active devices capable of generating mechanical motion of solids or fluids. Motion is generated via converting one form of energy (for instance electrical) into kinetic energy.

14.7 SUMMARY

- Micro Electro Mechanical Systems (MEMS), also written as micro-electromechanical the related micro mechatronics and microsystems

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constitute the technology of microscopic devices, particularly those with moving parts. They merge at the nanoscale into Nano Electro Mechanical Systems (NEMS) and nanotechnology.

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- MEMS became practical once they could be fabricated using modified semiconductor device fabrication technologies, normally used to make electronics.
- A capacitive MEMS switch is developed using a moving plate or sensing element, which changes the capacitance.
- Ohmic switches are controlled by electrostatically controlled cantilevers. Ohmic MEMS switches can fail from metal fatigue of the MEMS actuator (cantilever) and contact wear, since cantilevers can deform over.
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- Silicon also has significant advantages engendered through its material properties. In single crystal form, silicon is an almost perfect Hookean material, meaning that when it is flexed there is virtually no hysteresis and hence almost no energy dissipation.
- The electronics industry provides an economy of scale for the silicon industry, crystalline silicon is still a complex and relatively expensive material to produce. Polymers on the other hand can be produced in huge volumes, with a great variety of material characteristics.
- MEMS devices can be made from polymers by processes, such as injection molding, embossing or stereo lithography and are especially well suited to microfluidic applications, such as disposable blood testing cartridges.
- Metals can also be used to create MEMS elements. While metals do not have some of the advantages displayed by silicon in terms of mechanical properties, when used within their limitations, metals can exhibit very high degrees of reliability

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- The nitrides of silicon, aluminium and titanium as well as silicon carbide and other ceramics are increasingly applied in MEMS fabrication due to advantageous combinations of material properties.
- Porous silicon (abbreviated as 'PS' or 'pSi') is a form of the chemical element silicon that has introduced Nano pores in its microstructure, rendering a large surface to volume ratio in the order of 500 m^2/cm^3.
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- Piezo MEMS still face many difficulties that impede its ability to be successfully commercialized. For instance, the success of depositing uniform films of piezo electrics still depend heavily on the use of appropriate layers of proper nucleation and film growth.
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- Accelerometers are also used for machinery health monitoring to report the vibration and its changes in time of shafts at the bearings of rotating equipment's, such as turbines, pumps, fans, rollers, compressors.

14.8 KEY WORDS

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- **Micro Electro Mechanical Systems (MEMS):** It is the related micro mechatronics and microsystems constitute the technology of microscopic devices, particularly those with moving parts. They merge at the nanoscale into Nano Electro Mechanical Systems (NEMS) and nanotechnology.
- **Porous silicon:** Porous silicon (abbreviated as 'PS' or 'pSi') is a form of the chemical element silicon that has introduced Nano pores in its microstructure, rendering a large surface to volume ratio in the order of 500 m^2/cm^3.
- **Piezoelectric**: A piezoelectric Micro Electro Mechanical System (piezo MEMS) is a miniature or microscopic device that uses piezoelectricity to generate motion and carry out its tasks. It is a micro electro mechanical system that takes advantage of an electrical potential that appears under mechanical stress.
- **Piezo-resistive**: The piezo-resistive effect is a change in the electrical resistivity of a semiconductor or metal when mechanical strain is applied. In contrast to the piezoelectric effect, the piezo-resistive effect causes a change only in electrical resistance, not in electric potential.
- **Micro actuators**: Micro actuators are small-scale active devices capable of generating mechanical motion of solids or fluids. Motion is generated via converting one form of energy (for instance, electrical) into kinetic energy.

14.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Define the MEMS.
2. Explain the porous silicon based MEMS.
3. Analyse the silicon oxide based on MEMS.
4. Elaborate on the piezo electric.
5. Define the piezo resistive.
6. What do you understand by the micro- actuators?

Long-Answer Questions

1. Describe briefly about the state MEMS with the help of appropriate examples.
2. Explain in detail about the properties of silicon, porous silicon, and silicon oxide.

NOTES

3. Discuss about the fabrication of piezo-electric and piezo-resistive with the help of appropriate examples.
4. Explain the applications of micro actuators and micro accelerometer with the help of appropriate examples.

14.10 FURTHER READINGS

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